FINAL REPORT FOR NSG 5071

Laser Induced Photoluminiscence Studies of Primary Photochemical Production Processes of Cometary Radicals

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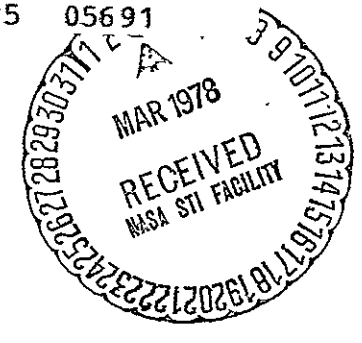


Abstract

A tunable vacuum ultraviolet flash lamp has been constructed. This unique flash lamp has been coupled with a tunable dye laser detector and permits the experimenter to measure the production rates of ground state radicals as a function of wavelength.

A new technique for producing fluorescent radicals has been discovered. This technique called Multiphoton Ultraviolet Photodissociation is currently being applied to several problems of both cometary and stratospheric intrest. Already it has been demonstrated that NO_2 will dissociate to produce an excited fragment and the radiation can possible be used for remote detection of this species.

Past Accomplishments

Several important advances have been made in the use of lasers to understand the photochemical processes that are occurring in the coma of comets. It has been theoretically shown[1] that the sun can be used, along with the space shuttle, as a photochemical light source to investigate in situe, which parent molecules could produce the observed cometary radicals. A new experimental technique "Multiphoton Ultraviolet Photodissociation" has been discovered and is in the process of development. Some of the experimental limitations of N_2 pumped dye lasers have been investigated and solutions for some of these limitations have been obtained. The combination of a vacuum ultraviolet flash lamp and a vacuum ultraviolet monochromator has been tested and found to perform according to the design specifications. In the balance of this proposal these advances will be discussed and an experimental plan for the coming year will be proposed.

One of the nagging problems about theoretical and experimental studies aimed at uncovering the physical and chemical mechanisms responsible for cometary emission is determining whether these mechanisms work in a space environment. The "ideal solution" to this problem would be a rendeavous flight to a major comet such as Halley or Encke. At the present time budgetary and time constraints do not permit scientists to use this solution. An alternate solution would be a space release of gas that is thought to be a possible parent compound of one of the cometary radicals. While this approach has been tried it has not been very

successful. The principal reason for this lack of success appears to be that the surface brightness of the cloud of free radicals is too low to be observed on earth.

We have investigated this problem and determined that a solution could be devised using laser technology and the space shuttle. We have proposed that NASA could release a gas from the space shuttle and use a tunable dye laser to probe it at different distances from the shuttle. The dye lasers spectral brightness is much greater than the spectral brightness of the sun. Suppose we have a dye laser that has a 10 mj output, 5×10^{-9} sec pulse width, a 0.1 Å bandwidth, and all in a 1 cm^2 area. This laser will have a spectral brightness of 5×10^{24} photons/sec cm^2 Å at 3000 Å. This is 10^{11} times brighter than the solar radiation in this wavelength region.

The dye laser can be tuned to one of the known ro-vibronic transitions of a cometary radical. If any radicals have been formed by solar photodissociation, they will then be electronically excited. At a latter time, determined by the natural radiative lifetime of this excited state, this radical decays to the ground by emitting a photon. Some of these photons will then be detected with a telescope and suitable electronics on the space shuttle. The details of this solar photochemical method have been published in a NASA report .[1]

We have shown that an ArF laser could be used to sequentially excite small molecules to electronic states that have at least twice the energy of a single 193 nm ArF laser photon.[2] This means that this energy may be used to study the photochemistry that occurs at both 193 nm and at 96.5 nm.

Although a preliminary report on this work has been prepared and submitted to Chemical Physics Letters for publication a few high lights are repeated here in order to emphasize the aspects of this work that may be important for comets.

Acetylene was photolyzed with the ArF laser and all of the observed emission came from excited CH radicals. No C_2 Swan emission was observed in this system. This is very good evidence that that the C_2H_2 molecule only absorbs two laser photons and thus does not have enough energy to dissociate via the following reaction.

(1) $C_2H_2 + 2h\nu \longrightarrow C_2(A^3\Pi) + 2H - 106{,}383\ cm^{-1}$

The absence of these bands is also good evidence that the acetylene molecule does not dissociate by reaction (2), which is spin forbidden, even though there is more than enough energy for this process.

(2) $C_2H_2 + h\nu \longrightarrow C_2(A^3\Pi) + H_2 - 70{,}323\ cm^{-1}$

Although there are no excited $C_2(A^3\Pi)$ state radicals formed in the C_2H_2, there should be a substantial amount of $C_2(X^3\Pi_u)$ state radicals formed by the following photochemical process.

(3) $C_2H_2 + h\nu \longrightarrow C_2H(X^2\Sigma) + H(1^2S)$

(4) $C_2H_2 + h\nu \longrightarrow C_2(X^3\Pi_u) + H(1^2S)$

(5) $C_2H_2 + 2h\nu \longrightarrow C_2(X^3\Pi_u) + 2H(1^2S)$

We intend to look for ground state C_2 using our tunable dye laser. Reaction (5) is unimportant for comets, but its effect can be sorted out from reactions 3 and 4 measuring the signal as a function of laser intensity. If we do not see any evidence for reaction (3) and (4) it is unlikely that these processes can be important in comets.

When the ArF laser was passed through C_2N_2 and ClCN a strong "immediate" emission from the $B^2\Sigma^+$, and D states of CN was observed. This emission is thought to be the result of the dissociation of a C_2N_2 or ClCN molecule that has absorbed two ArF laser photons. This process is not important for cometary studies in and of itself, since the sun does not emit many photons at 96.5 nm.

In addition to the immediate emission we have also observed a "delayed" emission. This "delayed" emission is thought to arise from triplet-triplet annhilation in the gas phase. The significant thing about this delayed emission is that the spectrum indicates the presence of a new band system of CN. We think that this new band system could possibly be from a quartet transition of this radical. While these transitions have been theoretically calculated, they have never before been experimentally confirmed. By identifying and analyzing this new band system we may be able to look for similar transitions in the spectrum of a comet. If the quartet radical is observed in comets then we would have a species, other than the ions, that must have been formed as a result of electron impact bombardment. The reason for this is that the only allowed dissociation for an excited singlet C_2N_2 molecule that can produce a quartet fragment has to result in the production of two quartet fragments. The lowest quartet state of the CN radical lie ~3.5 e.v. above the ground state. Photons with about 12.0 e.v. would be needed to produce an excited (C_2N_2) singlet molecule with enough energy to produce two CN radicals in the $X^4\Sigma$ state. The HCN molecule can only produce the quartet from an excited triplet state, since the H atom can not form any quartets.

A singlet-triplet transition is strongly forbidden for single photon absorption, but is allowed for electron impact excitation. These arguments illustrate how the observation of quartet emission in comets would throw additional light upon the physical and chemical processes that are present. states with energies higher than the enrgy of one ArF laser photon. This observation along with the fact that NO does not absorb at 193 nm shows that "Multiphoton Ultraviolet Photodissociation" is occurring.

The ArF laser work also shows that it might be used to measure trace components in the stratosphere by dissociative excitation of these components. Consider a molecule such as NO_2. This molecule has an absorption coefficient of $3 \times 10^{-19} cm^2$/molecule at 190 nm. From the work that we have already reported we would expect that the following two step excitation of this molecule would occur.

(1) $NO_2 + h\nu \longrightarrow NO_2^*$

(2) $NO_2^* + h\nu \longrightarrow NO_2^{**}$

The doubly excited NO_2^{**} molecule will have enough energy so that the following reactions may occur,

(3) $NO_2^{**} \longrightarrow NO(C^2\Pi) + O$

$\longrightarrow NO(A^2\Sigma^+) + O$

$\longrightarrow NO(D^2\Sigma^+) + O$

If this doubly excited NO_2 molecule is produced one should obtain emission extending from below the laser wavelength up to the visible region. Figure 1 shows the spectra of the fluorescence that was obtained when NO_2 was irradiated with the ArF laser. This spectra shows bands that arise from NO states with an energy that is higher than the energy of one ArF laser photon. This observation along with the fact that NO does not absorb at 193 nm shows that "Multiphoton Ultraviolet Photodissociation" is occurring.

In developing a dye laser for our studies on the wavelength dependence of photodissociation two vexing problems have occurred. One of these problems is the wavelength broadening of the dye laser output when the only efficient dye (BBQ) for this region (3840 Å to 3890 Å) was used. The other problem was the destruction of dye laser cells by the focused output of the N_2 laser. This latter problem, in addition to being troublesome, is expensive since these cells cost $250 each.

We have shown[3] that damage to the dye cell and degradation of the dyes is due to the presence of impurities and/or the formation of peroxides in the solvents used for the dyes. Procedures for purifying the solvents and removing these peroxides were devised and all solvents are now routinely purified and checked periodically for peroxides. This problem has vexed the scientists and laser manufacturers for a long time.

We have also had difficulty with power broadening in BBQ, a dye with very high gain. When power broadening occurs the power density of the N_2 laser on the dye cell must be reduced in order to obtain 0.1Å bandwidths with a single dye laser. This can be accomplished by reducing the N_2 laser power and not focusing the laser light as tightly in the dye cell. The adjustment of the laser bandwidth becomes a fairly tedious problem and the best solution is to use an oscillator - amplifier configuration for the dye laser. This type of dye laser is now commercially available and we are requesting funds for one of these dye lasers in this year's budget.

The performance of the vacuum ultraviolet monochromator flash lamp combination can be seen in figure 2. This figure contains laser induced spectra obtained with the full output of the flash lamp along with one

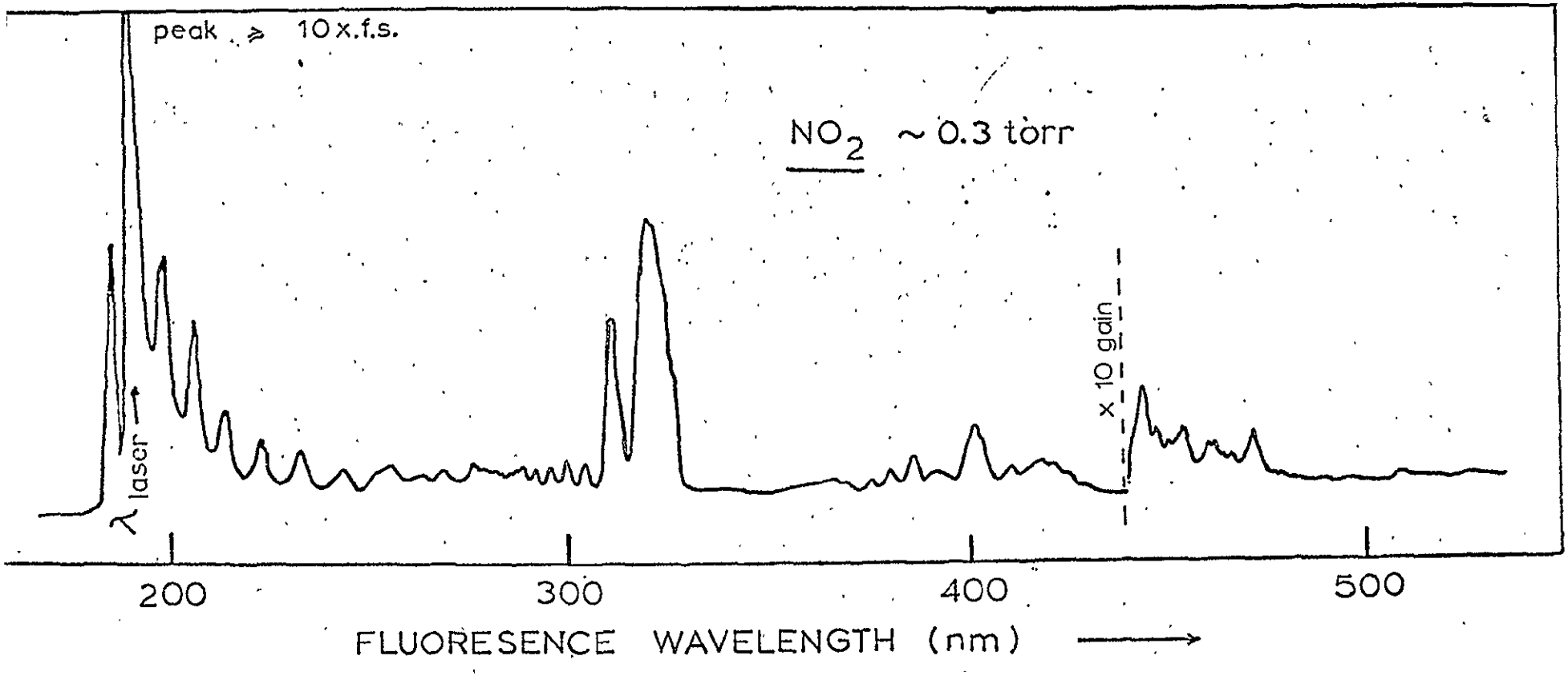
obtained with the vacuum u-v monochromator in place. The monochromator was tuned to the zeroth order so that its light has the same wavelength band as the flash lamp. The signal size with the monochromator is virtually the same as the signal size with the flash lamp. This is exactly what was predicted by the design studies that were discussed in our first proposal.

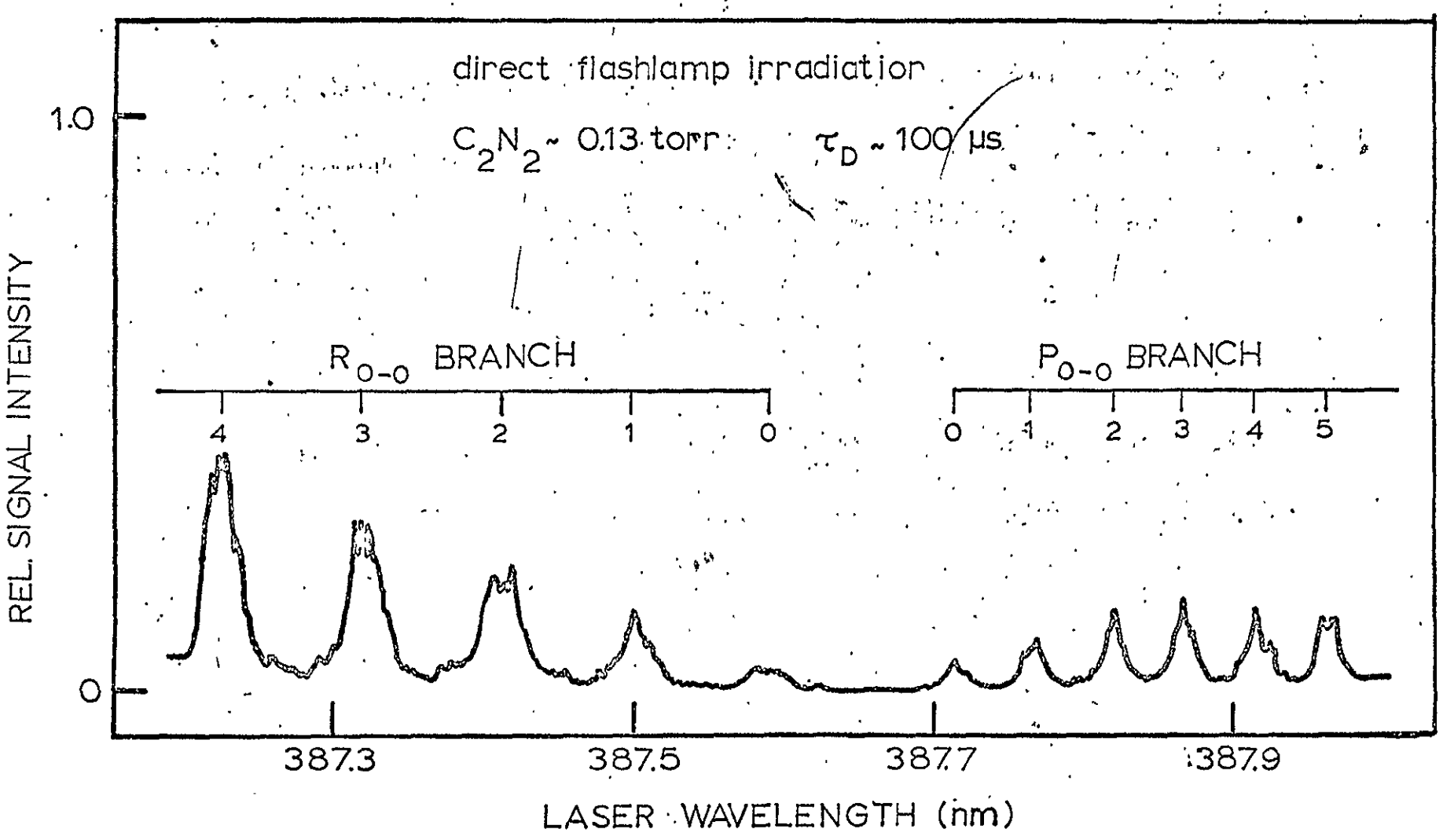
Figures

Figure 1. Multiphoton ultraviolet photodissociation spectra of NO_2. An ArF laser was used to obtain this spectra.

Figure 2. Tunable dye laser spectra obtained with the full flash lamp.

Figure 3. Tunable dye laser spectra obtained with the tunable vacuum ultraviolet flash lamp.


peak ≈ 10 x.f.s.
NO_2 ~ 0.3 torr
x 10 gain
λ laser
200
300
400
500
FLUORESENCE WAVELENGTH (nm)


direct flashlamp irradiation
C_2N_2 ~ 0.13 torr
τ_D ~ 100 μs
R_{0-0} BRANCH
4
3
2
1
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0
1
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REL. SIGNAL INTENSITY
387.3
387.5
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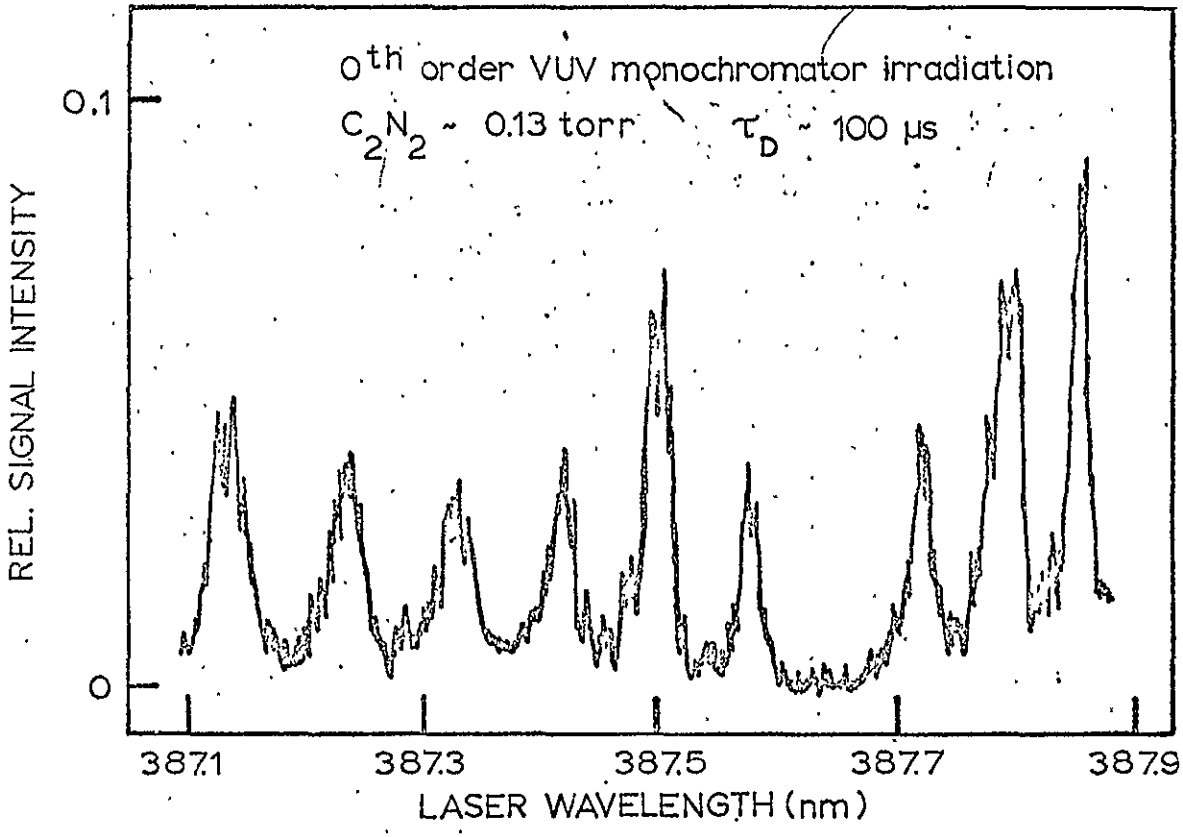
387.9
LASER WAVELENGTH (nm)


0th order VUV monochromator irradiation
C_2N_2 ~ 0.13 torr
τ_D ~ 100 μs
0.1
0
REL. SIGNAL INTENSITY
387.1
387.3
387.5
387.7
387.9
LASER WAVELENGTH (nm)

Multiphoton Ultraviolet Photochemistry

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We wish to report on a series of photolysis experiments at 193 nm using a 20 mj/pulse ArF laser. The laser wavelength is in a favorable region for dissociation of many small polyatomic molecules. The light emitted by the radical fragments is different from what is obtained when low intensity light sources are used to irradiate the same molecular systems. The kinetic origins of these differences have important implications for laser photochemistry.

If the molecule under study has an absorption spectrum which is relatively sharp, implying a long lived excited state, a significant fraction of the molecules can absorb two or more photons sequentially before dissociation. In this case, the laser pumping rate of the excited state is of the same order of magnitude as the unimolecular decay rate of this state. This leads to a more complicated photochemistry [1]. Excited states can be formed that have two or three times the energy of states produced when a single photon is absorbed. Further, since these states result from sequential absorption, they may also have different symmetries.

A schematic diagram of the apparatus used in this study is shown in Fig. 1. The essential point here is that the ArF laser was never focused into the observation cell. Thus, even though we have a fairly intense laser pulse, it is not strong enough to initiate processes such as simultaneous multiphoton absorption or dielectric breakdown. At no time did we see

the characteristic spark that is observed during dielectric breakdown of gasses.

The ArF laser was passed through the observation cell and excited the gas under study. Any fluorescence induced in the gas as a result of photodissociation, collisions or laser excitation, is observed at right angles through the J-Y holographic monochromator. The radiation is detected by a photomultiplier sitting behind the monochromator and the signal is processed with a boxcar integrator. The output of the boxcar integrator is recorded on a chart recorder as a function of the wavelength of the fluorescent light. In this manner the spectra shown in Figs. 2,3, and 4 were obtained. Latter runs used a flow system with a Granville-Phillips pressure controller to maintain constant pressure in the interaction volume. By slowly flowing the gas, a fresh sample was supplied to the interaction region for each laser pulse.

The spectra shown in Figs. 2,3, and 4 all show emissions from small molecules that require substantially more energy than is available from a single ArF laser photon. For example, 103,083 cm^{-1} of energy is required to form a CH ($A^2\Delta$) radical from C_2H_2. Since an ArF laser photon has only 51,813 cm^{-1}, two of these would be needed to produce the observed transition in acetylene. A similar situation is found for most of the other cases studied.

Presently the most plausible explanation of these results is that an excited molecule, formed in the initial photolysis, lives long enough to absorb a second photon. It will then have enough energy to produce the observed excited radicals.

Even this mechanism does not explain all of our results. Especially

higher states of the radical, that result in emissions near the laser line, are thought to be the result of direct laser excitation of a fragment radical. This is illustrated in C_2H_2, where the emission near 193 nm probably results from the laser excitation of $A^2\Delta$ CH radicals produced by dissociation of doubly excited acetylene molecules.

Detailed mechanisms will be proposed to explain each of the emissions shown in the figures. We will also present the results of laser intensity and pressure studies.

This work was supported by grants from NASA Number NSG 5071, from NSF Number MPS75-12848 and from ERDA Number E-(40-1)-5056.

Footnotes

1. "Competition Between Multiphoton Ionization and Multiphoton Fluorescence in NO," by William M. Jackson and Chung-San Lin. Submitted to Int. J. of Chem. Kinetics.

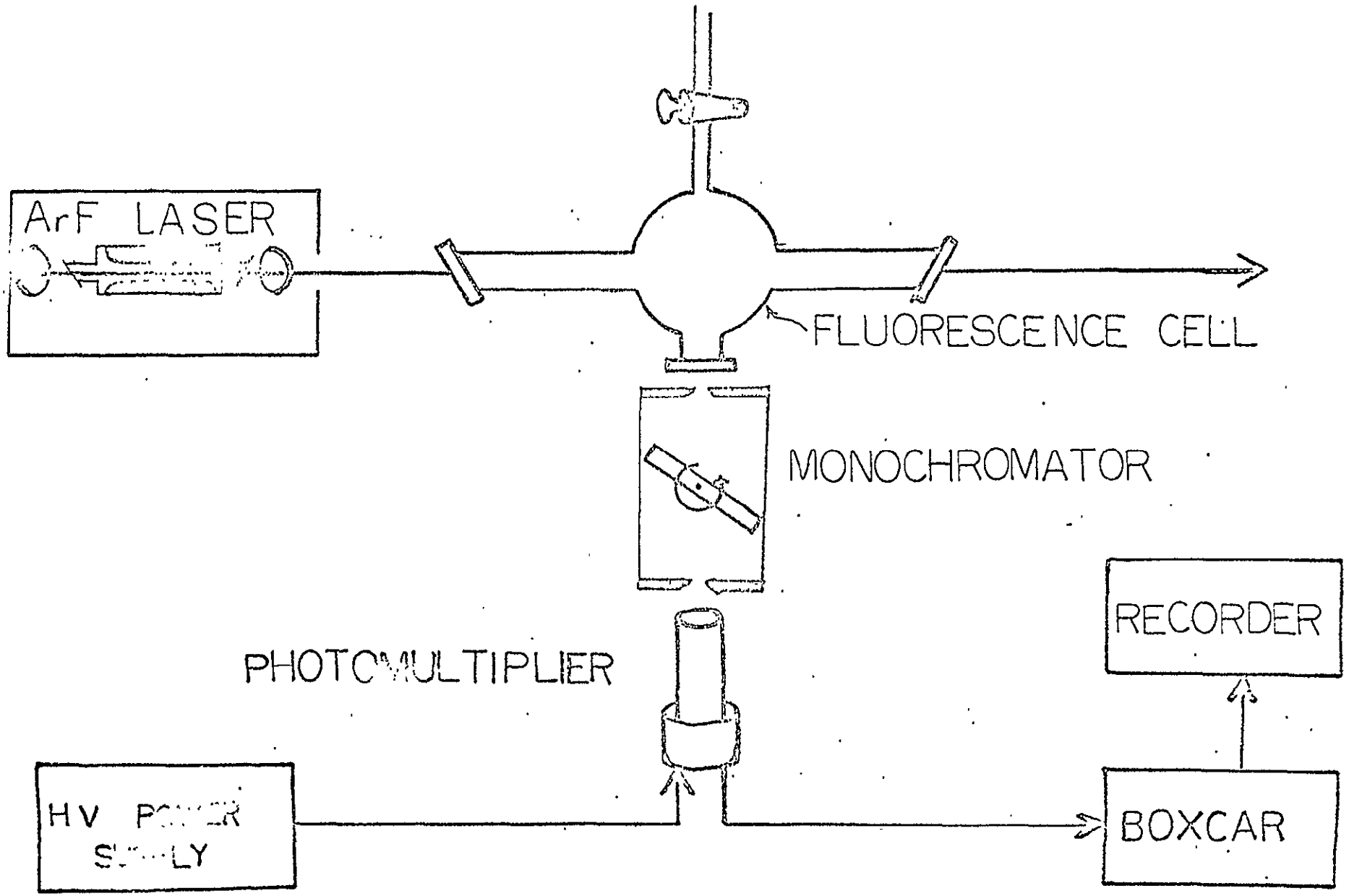
Figure Captions

Figure 1. Experimental Apparatus

Figure 2. Fluorescence induced by the multiphoton dissociation of hydrocarbons.

Figure 3. Fluorescence induced by the multiphoton dissociation of OH containing compounds.

Figure 4. Fluorescence induced by the multiphoton dissociation of CN containing compounds.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FLUORESCENCE CELL
MONOCHROMATOR
RECORDER
PHOTOMULTIPLIER
HV POWER SUPPLY
BOXCAR

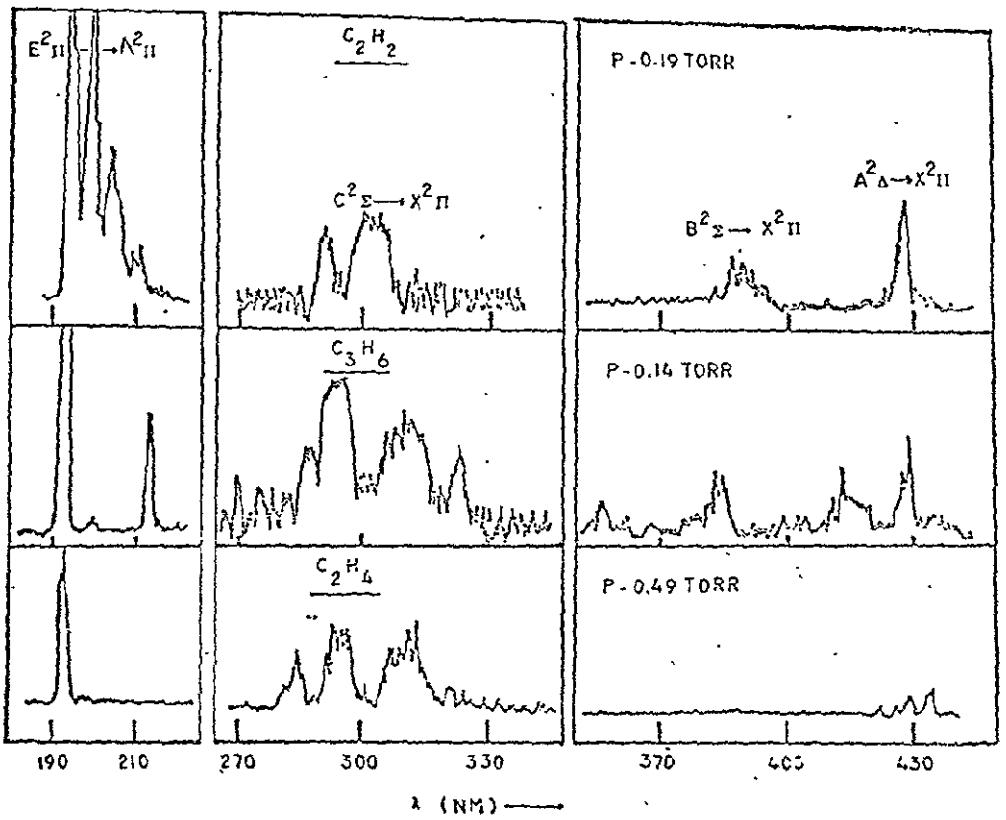
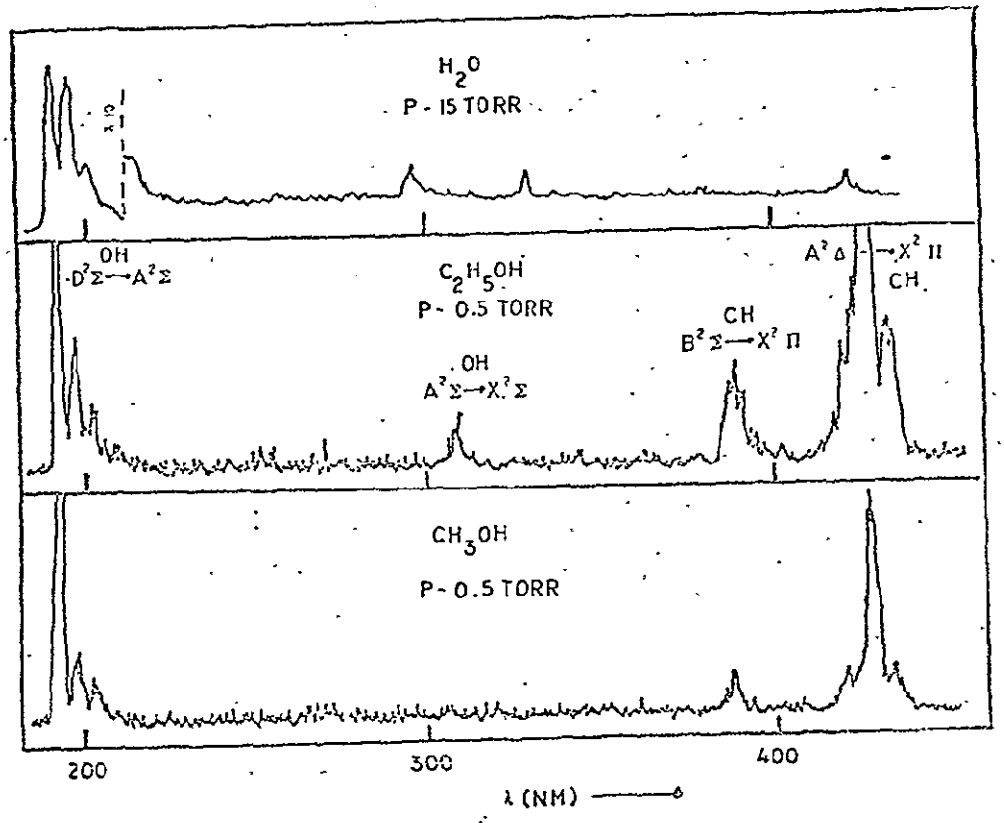


Figure 2. Fluorescence induced by the multiphoton dissociation of hydrocarbons.



gure 3. Fluorescence induced by the multiphoton dissociation of OH containing compounds.

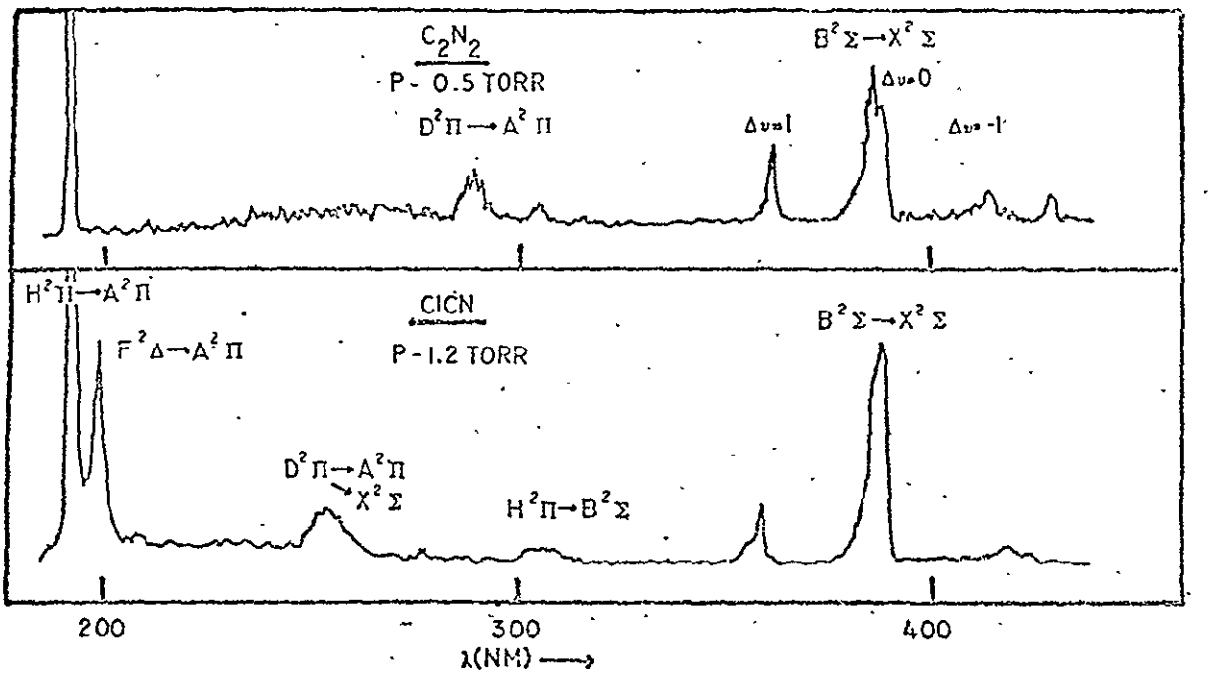


Figure 4. Fluorescence induced by the multiphoton dissociation of CN containing compounds.

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Multiphoton Ultraviolet Photochemistry

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Abstract

Multiphoton photodissociation has been observed in C_2N_2, C_2H_2, C_2H_4, CH_3OH, and C_2H_5OH. In all of these molecules fluorescence from small free radicals such as CN, CH, and OH has been observed. None of the observed fluorescence can result from the absorption of a single 193 nm photon. Arguments are presented which suggest that the observed results are best explained by invoking a sequential absorption scheme where the excited molecule absorbs a second laser photon rather than predissociating.

Emissions have also been observed when H_2O is photolyzed with the ArF laser. In H_2O the evidence suggests that this emission arises from collisional dissociation of two excited H_2O molecules.

Introduction

The commercial development of rare gas eximer lasers has opened up a new realm of photochemistry. The high intensity of these lasers will allow the photochemist to drive photochemical reactions at rates that compete with the unimolecular decay rates observed in low intensity photochemical systems. States that normally predissociate now may have an opportunity to absorb a photon and be driven to a higher excited state. We have already shown [1] that this type of competition occurs when a tunable dye laser is focused in NO, so that it would not be surprising to see similar phenomena when using the ArF laser. In this paper preliminary results that have been obtained with an ArF laser on a number of molecules are reported. These studies demonstrate some of the potential of this laser.

Experimental

The unfocused beam of an ArF laser was passed through a static fluorescence cell equipped with long baffle arms and suprasil windows. Any fluorescence induced by the laser was viewed at right angles to the laser beam through another suprasil window with a J-Y H20V monochromator. The monochromator had a band pass of 1 nm and the photons were detected with a R666S Hamamatsu photomultiplier tube. The electronic signal was processed by a PAR 162 boxcar analyzer and recorded on a strip-chart recorder. All of the gases that were used were purified by using freezing and pumping cycles with various slush baths. On some occasions more elaborate purification schemes were used.

Results and Discussions

The ArF laser induced identifiable fluorescence in ClCN, C_2N_2, C_2H_2, C_2H_4, CH_3OH, C_2H_5OH, HOH. No detectable fluorescence was observed from CH_4. All of the molecules that exhibit fluorescence absorb at 193 nm. Typical spectra obtained from each of these gases is shown in figures 1, 2, and 3. These results are surprising because the observed emissions could not result from the absorption of a single photon. In no case, is there enough to both break the bond and supply the observed excitation energy. Dielectric breakdown can not be invoked to explain the results because the laser was "not focused" and at no time was the characteristic light that results from this phenomena observed. Since static cells were used in all of this work, there is a possibility that some of the results were due to secondary photolysis of the intermediate products. This can explain some, but not all of the observed results.

The energetics for the production of various emissions may be used along with the fluorescence spectra and previous photochemical results to discuss some photochemical mechanisms that may be occurring in the various systems that have been studied.

ClCN

The ArF laser photons do not have enough energy to produce $B^2\Sigma^+$ state of CN by direct photodissociative excitation of this molecule. The threshold for B state production lies at 165 nm. The fact that such emission is seen must be due to either secondary absorption by the excited $ClCN^*$ molecule or by the CN fragments. The ClCN absorption spectrum shows no structure in the region of 193 nm [2]. This suggest that

the predissociation lifetime of the upper state is faster than its radiative lifetime [3]. The absorption of ClCN at 193 nm is fairly weak with an oscillator strength of only 2.5×10^{-3} [4]. Using this value one can compute that the natural radiative lifetime of this state is 2×10^{-7} sec. The predissociation lifetime of this upper state should be several orders of magnitude faster than the natural radiative lifetime. The lifetime for secondary absorption by the excited state depends upon the absorption coefficient and the light flux. The light flux of the 25 mj, 20 nsec pulsed ArF laser is about $7.5 \times 10^{+24}$ photons/cm^2 sec, so for an absorption coefficient of 10^{-17}cm^2 the lifetime for secondary absorption will be about 10^{-8} sec. This lifetime is of the same order of magnitude as the predissociation lifetime of excited ClCN* so that a significant fraction of these molecules can undergo further excitation.

An alternate explanation is that the CN radical produced by primary dissociation absorbs a laser photon and is excited to a high lying state which cascades downward, finally yielding B state emission. It is unlikely that this absorption starts from the $X^2\Sigma^+$ state of CN as only the upper vibrational levels of the $B^2\Sigma$ state could be reached from this state [5]. The Franck-Condon factors coupling these upper vibrational levels to the lower levels of the X state are highly unfavorable, mitigating against this process [6].

It is energetically possible at 193 nm to produce the $A^2\Pi$ state by direct photolysis of ClCN [7]. Low intensity vacuum ultraviolet photolysis studies of ClCN at wavelengths longer than 160 nm have shown that only X state radicals are produced [8]. Thus, there is no way that the observed results could be due to laser excitation of $X^2\Sigma^+$ radicals that are produced by one photon photodissociation.

C_2N_2

The dissociation of cyanogen by a 193 nm photon can only produce two $X^2\Sigma$ state CN radicals. One of the ground state radicals could have as many as 3 vibrational quanta, if all of the available excess energy went into vibrational excitation of only one of the CN fragments. Previous studies at shorter wavelengths on the C_2N_2 molecule have shown that most of the CN radicals are formed in the ground vibrational levels [9]. Direct laser excitation of these ground state radicals would result in the formation of $B^2\Sigma$ state radicals with about 12 to 15 vibrational quanta. The Franck-Condon factors for these transitions are below 10^{-15}, making this possibility highly unlikely.

The observations in figure 1 could result from an excited C_2N_2 molecule absorbing a second laser photon and then dissociating to produce excited B state radicals. The presence of well defined bands in the absorption spectrum of C_2N_2 at 193 nm support this conclusion[10].

C_2H_2

The absorption spectrum of acetylene at 193 nm has well developed vibrational structure [11], implying that there is sufficient time at high intensities to absorb a second photon. Some early photochemical studies agree with this suggestion [12]. We have analyzed our observations to see if they agree with one or both of these models.

Most of the bands shown in figure 2 may be assigned to the CH radical. In order to produce ground state CH radicals by single photon absorption the energy of the photon must be greater than 79,866 cm^{-1}. However, ground state CH radicals can not absorb light at 193 nm because there are no transitions for the radical at this wavelength [13]. The lowest electronic state of the radical that can absorb a laser photon is the A state, but 106,014 cm^{-1} of excess energy are required to simultaneously produce an A and X state CH radical from C_2H_2. It is possible to obtain this energy from sequential excitation of acetylene or by secondary photolysis of any C_2H radicals produced in the primary step. One needs 69,177 cm^{-1} to produce $CH(A^2\Delta)$ radicals by photolysis of the C_2H radicals in the ground state. Secondary photolysis of the C_2H fragments is only possible if they are created with $\sim$17,000 cm^{-1} of internal excess energy. This does not seem likely, since experience has shown that a significant amount of energy appears as translational energy between the fragments during photodissociation [8,9,14]. Thus we conclude that the observed fluorescence is probably produced by sequential excitation of acetylene followed by the dissociation of the doubly excited molecule to produce both X and A state CH radical fragments. The A state CH fragments will be further excited by a third laser photon to the G state. The radicals in the G state can then cascade downward to form the F, E, D, and C states of CH.

We believe that the bands near 200 nm are due to the $G \longrightarrow A$ and $G \longrightarrow B$ transitions. The emissions from 270 to 350 nm are probably due to the C to X transition, while those seen at 350 nm and 430 nm are due to the $B \rightarrow X$ and $A \rightarrow X$ transitions respectively.

C_2H_4

Contrary to the case of acetylene, in ethylene only C⟶X fluorescence and the A⟶X emission is observed. Moreover, the distribution of the C⟶X fluorescence is different in the two cases. The absence of any bands that can be assigned to the other electronic states of CH argues against the direct production of A state radicals, since they would be expected to absorb a laser photon and exhibit evidence of all of the transitions seen in acetylene. An alternate explanation is that the ethylene molecule absorbs two photons sequentially to reach an excited state which dissociate to produce excited C state radicals. The absorption spectra of ethylene at 193 nm shows some vibrational structure supporting this explanation. The lowest energy process that can produce $CH(C^2\Sigma)$ radicals also produces CH_3 radicals. This reaction requires an energy of 88,747 cm^{-1} which is substantially less than the energy available from two 193 nm photons [15].

CH_3OH

Two strong emission bands are observed in the photolysis of this molecule. One occurs at 431 nm and has been assigned to the $A^2\Delta \longrightarrow X^2\Pi$ transition of the CH radical. A weaker emission at 389 nm has been attributed to the $B^2\Sigma \longrightarrow X^2\Pi$ transition of CH.

The other strong band system falls near the 193 nm wavelength of the laser. It is not due to scattered laser light since it shows structure, which the laser does not possess. In addition, it is much stronger than the scattered laser light seen when pure CH_4 was irradiated at the same pressure. The observed signal must therefore be due to some photochemical process in the methanol vapor.

The emissions could be from $E \rightarrow A$ and/or $F \rightarrow A$ transitions in CH. If this were the case one would expect to find $C \rightarrow X$ fluorescence as a result of radiation cascades. Since no such fluorescence was observed we believe that a better explanation is the direct laser pumping of the $A^2\Sigma^+$ state of an OH fragment to the $D^2\Sigma$ state. Because of the long (1μs) lifetime of the $A^2\Sigma^+$ state, and the relatively high pressure in the experimental cell it would be difficult to observe the $A \rightarrow X$ fluorescence, from OH.

The lowest thermodynamic thresholds for production of $CH(A^2\Delta)$ $CH(B^2\Sigma^-)$ and $OH(A^2\Sigma^+)$ radicals from CH_3OH are 90,374 cm^{-1}, 92,855 cm^{-1}, and 63,274 cm^{-1} respectively, all of which are substantially larger than the energy of a single ArF laser photon [15]. The only way that these processes could occur is by sequential absorption of two photons or secondary photolysis of free radicals produced in the primary step. Based on previous low intensity photolysis studies in this region we prefer the mechanism of sequential absorption. These studies suggested that there observed products were due to collisionally induced dissociation [16]. This means that the state initially produced lives long enough for collisions to take place. In such a long lived excited state predissociation can not compete with laser pumping to a higher excited state.

C_2H_5OH

The similarity between the observed emission in ethanol and methanol suggest that the same explanation can be used for both cases. This is not surprising, since for both molecules it is the $n \rightarrow \sigma^*$ transition that is excited [13]. Absorption in the region of 193 nm is weak, which implies that the transition has some forbidden character. [15]. This coupled with the fact that only weak predissociation occurs in the similar methanol bands

(see the previous discussion and Ref. 16) suggests that the fluorescence is the result of sequential absorption followed by dissociation into CH radicals in the $A^2\Delta$ and $B^2\Sigma$ states.

As in methanol the structure near 200 nm results from the laser excitation of $A^2\Sigma^+$ state OH fragments. Here we do observe some weak $A \longrightarrow X$ fluorescence from OH in spite of the long lifetime and substantial quenching at 0.5 torr.

HOH

At low pressures, of the order of one torr or less, no emission was seen upon irradiation. At higher pressures above 10 torr the same emissions observed in CH_3OH and C_2H_5OH near 200 nm were detected. Since the laser intensity does not increase there is no other way to explain this result except by invoking a collisional process. In light of the fact that when CH_3OH is irradiated by a weak source it undergoes collisionally induced predissociation when the $n \rightarrow \sigma^*$ transition is excited and this is the same system excited in H_2O, one can reasonably expect that collisions of excited water molecules are involved in producing the emissions at 200 nm. The thermodynamic threshold for the production of $A^2\Sigma^+$ OH radicals is 73,710 cm^{-1} or 22,000 cm^{-1} greater than that available from the laser photons. This means that at least two excited water molecules must be involved in any collisional dissociation. As a result of such a collision an $A^2\Sigma^+$ OH radical would then be produced. This radical could be further excited by the laser to the $D^2\Sigma$ state which radiates, producing the observed spectra at 200 nm.

Conclusion

In the present work, evidence has been presented which shows that sequential excitation of molecules competes with one photon photodissociation in intense laser fields. We have also demonstrated in one of these systems that two excited molecules collide leading to dissociation of one of the collision partners. All of the evidence in the present studies point to the importance of including these types of effects in any study of laser induced chemistry.

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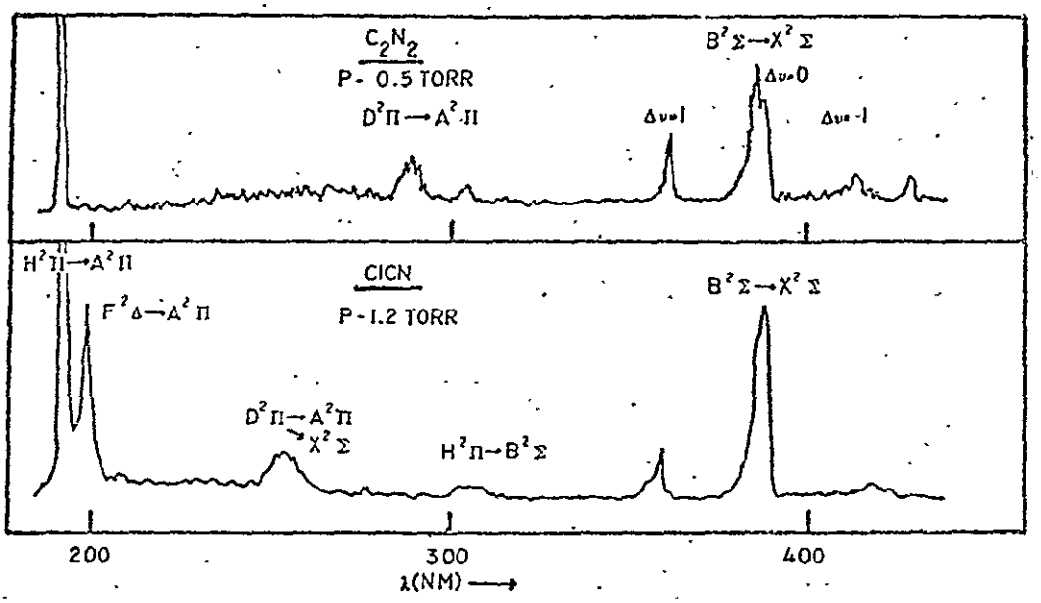

FIGURE 1.

Flourescence Spectra excited by the Multiphoton Ultraviolet Photo-dissociation of CN Containing Compounds.

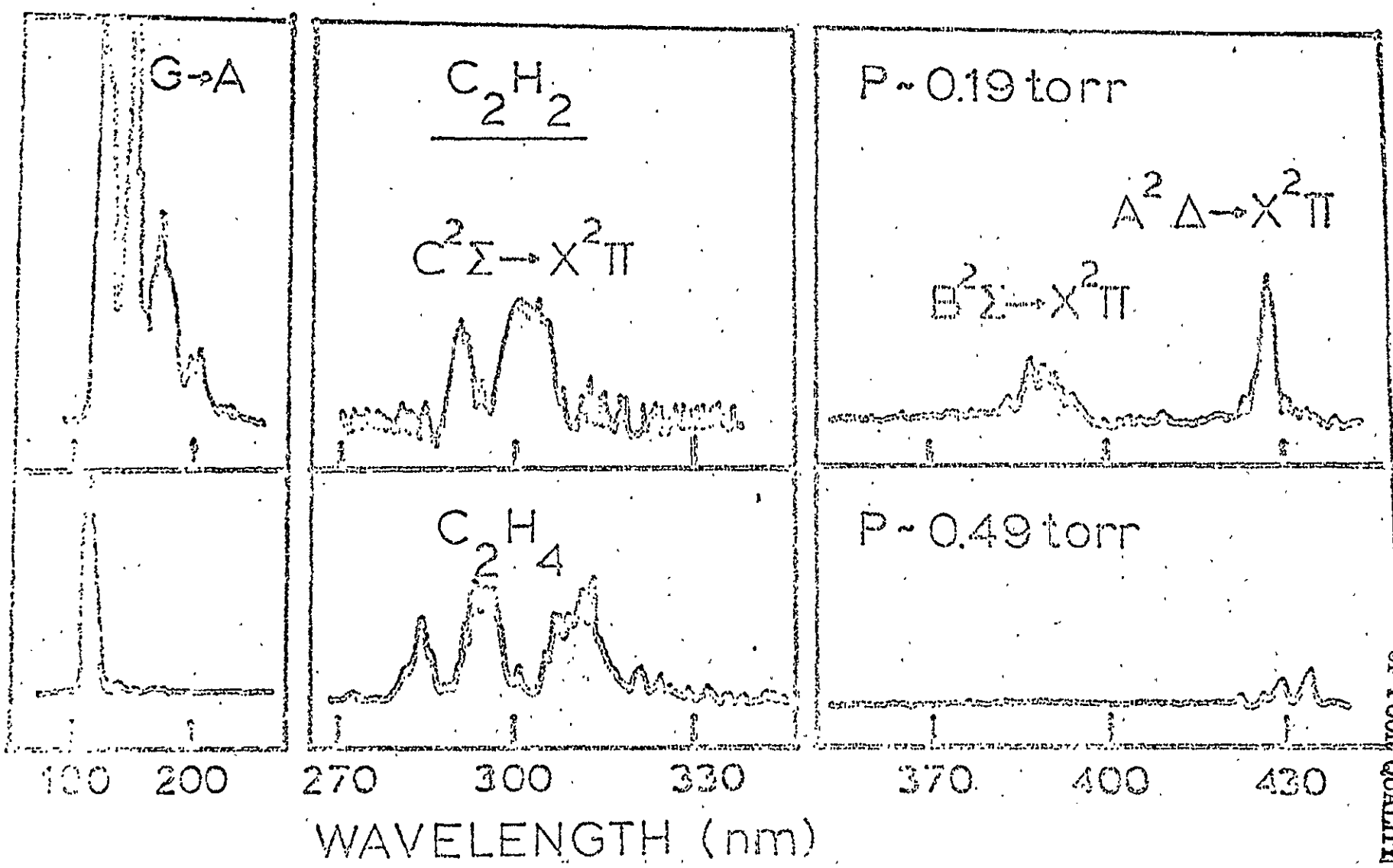

FIGURE 2

Fluorescence Spectra excited by Multiphoton Ultraviolet Photodissociation of Multiple Bonded Hydrocarbon.

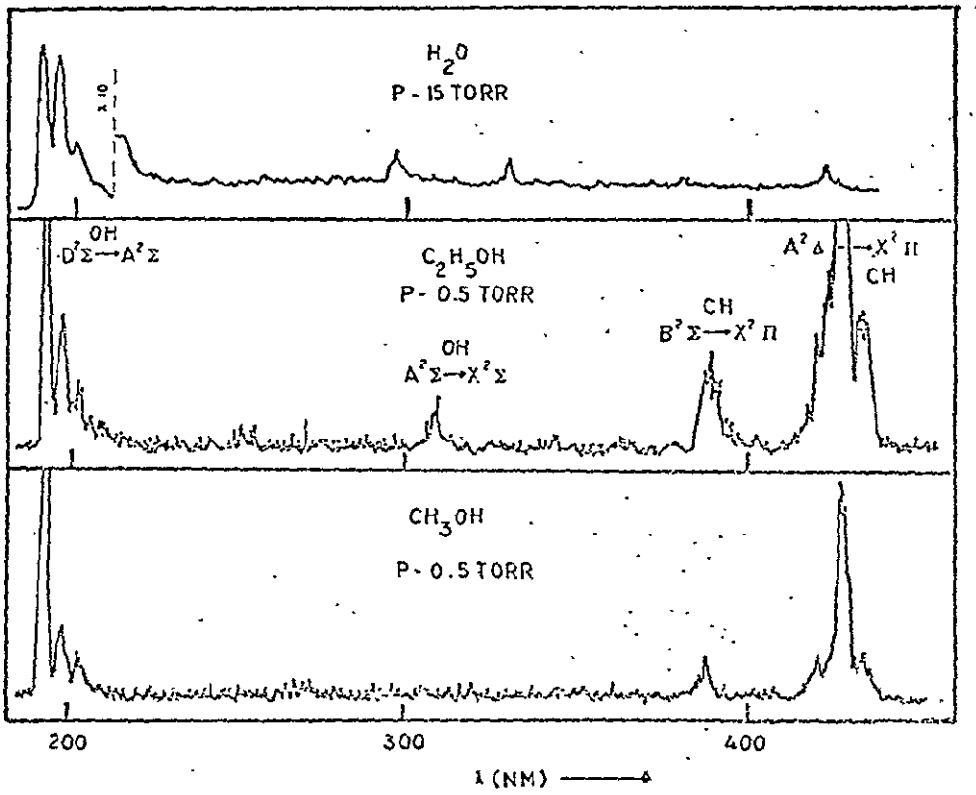

FIGURE 3

Fluorescence Spectra excited by Multiphoton Ultraviolet Photodissociation of OH Containing Compounds.

Appeared in the PROCEEDINGS OF THE SHUTTLE-BASED COMETARY SCIENCE WORKSHOP

SOLAR PHOTOCHEMISTRY USING THE SPACE SHUTTLE

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ABSTRACT

A continuing source of difficulty in cometary astrophysics is understanding the origin of C_2, C_3, NH and CO^+ species in comets. We propose an experiment to investigate these problems by continuously releasing suspected parent gases from the space shuttle and using a dye laser to selectively excite fragments produced as a result of solar photochemical decomposition of the molecules. The backscattered fluoresence will be gathered by a telescope, spectrally filtered and measured as a function of time after the laser pulse. We show that for reasonable estimates of the dissociation rate the expected signal is roughly described by $N_p(t) = N_o \exp[-t/\tau]$ for $t/\tau<10$, τ being the radiative lifetime of the daughter species, and typically of the order of 10^{-6} to 10^{-7} seconds. N_p is the number of photons reaching the detector per channel of width τ. N_o is calculated to be $\sim 10^6$. Thus the signals to be expected per pulse can be measured by analog techniques and the success of the experiment seems highly probable.

Introduction

A continuing source of difficulty in cometary astrophysics is understanding the origin of C_2, C_3, NH, and CO^+ species in comets. The C_2 and the NH radicals present difficulties because the most likely parents, ammonia and acetylene, do not form these radicals in a single photochemical process at the available solar wavelengths.[1] Further, since the observed emissions originate from triplet levels of the radicals it can be shown[1] that photodissociation through absorption of a single photon would violate selection rules and thus be unlikely to occur. The only currently reported single step photolysis source[2] of the C_3 radical is a minor product in the laboratory photodissociation of HC_2CH_3.

Substantial progress has been made in applying the results of laboratory studies to increase our understanding of photochemical processes that can occur in comets. Even with the reported progress and the prospects for future detailed studies there will always be difficulties associated with translating the laboratory results to the solar environment outside the earth's atmosphere. First, in the space environment there are no walls to complicate the interpretation of the results. Secondly, the time between collisions is orders of magnitude longer than it is in the laboratory, so that slow secondary processes can compete with the direct chemical reaction of these very liable species.

An ideal experiment would involve the release of suspected parent molecules one astronomical unit away from the sun in the interplanetary media. This ideal condition can not be met even in the proposed experiment, since the space shuttle does not reach interplanetary altitudes; it does of course operate at one astronomical unit.

In this proposal it will be shown that using the space shuttle one can obtain much of the needed information about photochemical processes that occur in comets by doing time resolved studies of the laser induced emission from the solar photodissociation fragments.

Proposed Space Shuttle Experiment

The proposed experiment consist of continuously releasing a gas from the space shuttle and using a pulsed tunable dye laser to selectively excite the fragments produced as the result of solar photochemical decomposition of the molecules. The collision time between molecules at the space shuttle's altitude is of the order of 13 seconds, thus a typical molecule will travel roughly 13 km before colliding with the ambient background gas. Any product formed by dissociation must be detected in times short compared to the collision time in order to insure that none of the observed products have been formed by collision with the ambient gas. Detection of the induced fluorescence as a function of both time and the laser wavelength will yield the rate of production of the species formed, the identity of the species, and the quantum mechanical state the species is formed in.

The spectra in Figure 1 is an example of the type of spectra that one can expect to obtain using laser induced fluorescence of the unstable species. This particular spectra is for CN radicals, but comparable spectrum may be expected for C_2, C_3, NH, and CO^+ species. It is important to be able to scan over a wide wavelength range, since a priori, we have no way of knowing exactly which rovibronic levels of the molecules are produced by the photodissociation process. In fact, determination of the rovibronic levels that the cometary radicals are produced in by solar radiation is valuable information and one of the aims of this ex-

periment. For example, this information can be used in explaining anomalies observed in the cometary spectra of the C_2 radical. The spectra of these radicals are well separated, so that there will be no problems of interpretation caused by overlapping lines and bands.

The 13 second exposure time of the parent molecule to solar radiation is short compared to the times that occur in comets. The calculated photochemical lifetimes for NH_3, C_2H_2, and HC_2CH_3 in cometary bodies at one astronomical unit have been reported as 2000, 5000, and 5000 sec respectively.[1] Thus one in 150 to 400 is a crude estimate of the fraction of the parent molecules decomposed during a 13 second exposure time. The success of the proposed method for studying the photochemistry of parent molecules relies on the extreme sensitivity of the laser technique. It has been reported[3] that in the laboratory one can detect densities as low as 10^5/cc or about 10^{-14} atm. We propose to use this high detection sensitivity to determine the mechanism for solar photodissociation of the proposed parent molecules.

Calculated Signal Strengths

In any fairly sophisticated experiment one should make a good estimate of its probable success and an evaluation of what will be learned if no signal is detected with all of the systems functioning. If no signal is detected, then one can conclude that acetylene, propyne, and ammonia are not the photochemical precursors for C_2, C_3, and NH in comets. This in turn would strongly suggest that collisions are the primary production mechanisms for these species or that some exotic molecule is the parent of these radicals. If forced to this last alternative then we must conclude the enviroment where comets are formed is stranger than is

currently believed.

The density of radicals formed from the photodissociation of a parent molecule has been computed by Haser.[4] The equation[5] he obtained for a freely expanding gas is,

$$\rho = \rho_o (u_o / u_1)(r_o/r)^2 \beta_o/(\beta_1-\beta_o)(\exp(-\beta_o x) - \exp(-\beta_1 x)) \quad (1)$$

In this equation ρ is the density of the daughter molecule and ρ_o, the number density of the parent molecule. The β is the inverse of the mean distance traveled before dissociation which is the product of the flow velocity u, of the molecule times its lifetime τ, at one astronomical unit. ρ_o is the number density of the parent molecule, i.e., at the distance r_o. While it will not be possible to put a true artificial comet in space this equation can be adapted to our use if it is realized that r_o refers to a characteristic dimension of the emitter, such as the gross dimensions of a linear array of holes through which the gas is allowed to effuse. This equation then gives the lower limit of the radical density. If the parent molecules are released in such a way that one obtains a more directed flow, such as with nozzels[6] or multicappilary arrays,[7] the observed radical density could be much higher.

We can simplify the above equation since the argument of the exponential will be small for values of x less than 13 kilometers and $u_o\tau_o$ is much less than $u_1\tau_1$. There is both theoretical and observational evidence that the latter assumption is valid. O'Dell and Osterbrook[8] have determined the values of these products for the C_2 radical and found that they differed by an order of magnitude. The symmetry of Haser's equation does not, however, allow one to determine which of these values are larger. Jackson[1] in a recent review has calculated the photochemical lifetime of acetylene and has shown that it is of the order of 5000 seconds.

This is in reasonable agreement with the lowest determined lifetime of 10^4 sec of O'Dell and Osterbrook. The highest lifetime determined by these two authors is 100,000 seconds, forcing one to conclude that this is the lifetime of the C_2 daughter. The NH, C_2, and CN radicals probably all have lifetimes that are longer than their parents, since the suspected parent molecules will have a weaker bond than the daughters and therefore require longer wavelengths for photodissociation. The solar intensity[9] rises rapidly as the wavelength is increased from 100 nm to 300 nm, which will substantially reduce the photochemical lifetime of the parent relative to the daughter. Assuming that the daughter and parents have about the same flow velocities then β_o will be much greater than β_1.

The assumptions given in the above paragraph can be used to simplify to,

$$\rho = \rho_o(r_o^2/u_o\tau_o) \quad (x/r^2) \tag{2}$$

The laser pulse width is much smaller than the radiative lifetime of the excited radicals so that only a negligible fraction of these radicals will radiate while the laser is on. Under these circumstances the rate of laser excitation for an optically thin gas in which stimulated emission may be neglected can be calculated from equation 3.

$$d\rho^* / dt = \sigma I \rho \tag{3}$$

In this equation ρ^* is the number density of the excited state, σ is the absorption coefficient of the radical, and I is the laser intensity in photons /cm^2 sec. Equation 3 may be multiplied by the cross sectional area, A_o, of the laser beam to yield an expression for N^* the number of excited molecules produced per unit path per sec.

(4) $dN^*/dt = \sigma I \rho A_o$

This differential equation only applies when the laser is on. Assuming the laser intensity is constant for a time t_o, then equation 4 may be integrated to yield.

(5) $N^* = I\sigma\rho A_o t_o = E\sigma\rho / h\nu$ where: E=energy of laser pulse
ν=laser frequency

When the laser pulse has passed a segment of length dr the excited molecules decay at the rate

(6) $$\frac{dN^*(r)}{dt'} = \frac{N^*}{\tau} = \frac{1}{\tau}\,\frac{E\sigma}{h\nu}\,\rho(r)\,\exp(-t'/\tau)$$

where τ is the radiative lifetime (in this experiment the effect of collisions upon the de-excitation of the molecules is negligible), and t', the local time at the segment centered about r, is less than $t-t_o$ and greater than $2r_o/c$, t being the time as measured at the detector. The number of photons received per centimeter per second by the detector from this segment is the rate of emission multiplied by the solid angle of the segment subtended by the detection system or

(7) $$\phi(r,t)\,dr\,dt = \frac{1}{\tau}\,\frac{E\sigma}{h\nu}\,\frac{A\rho(r)}{4\pi r^2}\,\exp\left[-(t - t_o - 2r/c)/\tau\right]\,dr\,dt$$

$\phi(r,t)$ is thus the contribution of a segment at r, where $c(t - t_o)/2 > r > r_o$, to the signal at time t. The rate at which the photons reach the detector from all excited molecules, $dN_p(t)/dt$ is, from eqs. (2), (5), and (7)

$$(8)\qquad \frac{dN_p(t)}{dt} = \Phi_o\left\{\int_{r_o}^{a} dr\,\frac{(r-r_o)(t-2r/c)}{r^4} + \int_{r_o}^{b} dr\,\frac{r-r_o}{r^4}\exp[-(t-t_o-2r/c)/\tau]\right\}$$

where

$$\Phi_o = \frac{1}{\tau}\,\frac{E\sigma}{h\nu}\,\rho_o\,\frac{r_o}{v_o\tau_o}\,\frac{A}{4\pi}\;;\; a = ct/2;\; b = c(t-t_o)/2$$

A is the area of the telescope.

The first integral is the contribution of the segment overlapped by the laser pulse and equals

$$(9)\qquad L = \frac{2t_o}{c^2t^2}\left(1 - 2\,\frac{r_o}{ct}\right)$$

Now t_o is short compared to τ and all other significant times considered in this calculation and so as $t_o \to o$ L disappears. This must happen since in order to derive eq. (5) we had assumed that no excited molecules will fluoresce during the time it takes for the laser pulse to pass through the region dr about position r. The integral L is small compared to B and may be neglected.

The second integral

$$(10)\qquad B = \frac{8}{3}\,\frac{r_o}{c^3t^3} - \frac{1}{3r_o^2} + \left(1 - \frac{2}{3}\,\frac{r_o}{c\tau}\right)e^{-t/\tau}\left[\frac{1}{2r_o^2} + \frac{1}{c\tau r_o}\right] + \frac{2}{c^2\tau^2}\left[Ei\left(\frac{t}{\tau}\right) - Ei\left(\frac{2r_o}{c\tau}\right)\right] - \frac{2}{c^2t}\left[\frac{1}{t} + \frac{1}{\tau}\right]$$

where Ei (x) is the tabulated exponential integral. This can be simplified

by neglecting terms where appropriate ($2r_o/c\tau$ for example) and by defining $\alpha(x)$ as

$$\alpha(x) = \frac{Ei(x)}{\left[\frac{e^x}{x}\right]} \qquad x>2 \; ; \; \lim_{x\to\infty} \alpha(x) = 1$$

Then

$$(11) \qquad B \approx e^{-t/\tau}\left[\frac{1}{6r_o^2} + \frac{1}{c\tau r_o} + \frac{2}{c^2\tau^2}\ln\left(\frac{c\tau}{2r_o}\right)\right] + \frac{2}{c^2\tau t}\left[\left(\alpha\left(\frac{t}{\tau}\right)-1\right) - \frac{t}{t}\right]$$

The gatewidth, of the detection system t_g, the radiative lifetime, τ, of the laser all limit the ultimate depth resolution ΔR of a LIDAR experiment. Kiddal and Beyer have defined ΔR by

$$(12) \qquad \Delta R \equiv (c/2)\,(t_o + \tau + \tau_g)$$

The radiative lifetimes of the radicals that will be studied in the present experiments is much greater than both t_o and τ_g so that ΔR is effectively $(c\tau)/2$.

The number of photons, N_p, reaching the detector per pulse in the interval from t to $t + t_g$ is from eqs (8) and (11)

$$(13) \qquad N_p(t) = \frac{t_g}{\tau}\,\frac{E\sigma}{h\nu}\,\frac{A}{4\pi}\,\frac{r_o\rho_o}{v_o\tau_o}\,B(t)$$

All of the quantities in this equation are known or can be calculated from known quantities. The only quantity that presents any particular difficulty

is σ, the absorption coefficient of the radical that one would like to detect.

The absorption coefficient for a single line is defined[10] by the following equation,

$$(14) \qquad I(\nu)I_o = \exp[-k\nu x] = \exp[-\sigma\rho_A x]$$

but $\int k\nu d\nu = (h\nu_o/4\pi)\, B_{nm}\, \rho_A(1-\rho_{A*}/\rho_A)$

where: B_{nm} = Einstein B coefficient for the transition

ρ_A = density of molecules in the J" rotational level

ρ_{A*} = density of excited molecules

For a line limited by Doppler broading one can integrate over the line profile and solve for B_{nm} in terms of the oscillator strength f. This then will give[10]

$$(15) \qquad \sigma' = k_o/c_A = [2/(\Delta\nu_D)][\ln 2/\pi]\ 1/2\ [\pi e^2/mc]f$$

This equation is valid for an atomic line, however for a molecular line f must be replaced[11] by $f_{nm}q_{v'v''}\, S_J/(2J''+1)$. The σ' can be converted to an absorption coefficient, σ, defined in terms of the total number density by multiplying by the fraction, $F_{J''}$, of the molecules in a given J" level and by the ratio of $\Delta\nu_D/\Delta\nu_l$ to account for the fact that the line width is determined by the laser line width.

$$(16) \qquad \sigma = (2/\Delta\nu_D)(\Delta\nu_D/\Delta\nu_l)\ [\ln 2/\pi]\ 1/2\ [\pi e^2/mc][f_{nm}q_{v'v''}\, S_J/(2J''+1)]F_{J''}$$

The oscillator strengths f_{nm}, Franck-Condon factors $q_{v'v''}$, and rotational line strengths S_J for the C_2 and NH radicals have all been measured so that they

present no particular difficulty in evaluating σ. The fraction of the molecules that are formed in a given J" level will be more difficult to determine since it is well known that free radicals are not necessarily rotationally equilibrated when produced by photodissociation. Recent experiments by the author[12] and his co-workers have shown that at least for some CN parent compounds the CN radicals initial rotational distribution may be characterized by a Maxwell-Boltzman distribution function with a high rotational temperature. This phenomena is illustrated in the plots in Figure 2. In light of these experiments it appears that $F_{J"}$ may be calculated from the Maxwell-Boltzman distribution function if a high rotational temperature is assumed. We will use this approach and assume a rotational temperature of 5000°K.

We are now in a position to estimate N_p for a given J" level of the C_2 or NH radicals using measured constants for these radicals along with assumptions about the experimental configuration. Figure 3 is a schematic drawing of how the laser transmitting and receiving telescope might look. We will assume that the receiving telescope is approximately 10" in diameter. We will further assume that the ρ_o at r_o is 10^{13} mole/cm^3 and that $r_o \sim 250$ cm. Both of these latter quantities could be obtained with a long arrays of supersonic nozzels[6] or multicappillary arrays[7]. If either of these devices are used to release the gas then it will minimize the amount of gas that has to be carried on the space craft and released for the experiment.

The density at r_o was obtained by the following consideration: in a gas release system that is 3 cm high and 450 cm long the area from which gas is released is 1350 cm^2. Assuming we can carry 1.35×10^4 gms of gas and that the flash lamp will only last for 10^6 shots, this will limit the observation time to about 28 hours for the pulse rate of 10 cps. The flux of gas released

if the average molecular weight is 30 AMU is 2×10^{18} molec/cm^{2}sec corresponding to a density of 4×10^{13} molec/cm^3.

Figure 4 gives the results for the photons arriving at the telescope per laser shot for the maximum J" level of the NH and C_2 ground states. This figure shows that one can easily detect the resonance backscattered photons from the NH and C_2 radicals produced by the assumed solar photodissociation of either C_2H_2 or NH_3. Further there is a great deal of flexibility in the proposed system, since higher σ_o may be obtained by releasing higher fluxes of the gas. Higher fluxes would permit us to look for even slower photodissociation processes and put firmer limits on the lifetimes of C_2H_2 and NH_3 in the solar radiation field.

The results in Figure 4 assume dye laser energies of the order of 10 millijoules per pulse of 0.1 A°. Recently, Davis and co-workers[13] have reported laser energies of this order of magnitude and bandwidths an order of magnitude smaller than 0.1 A° The laser they used to pump the dye laser was a frequency doubled Nd-Yag laser made by ILS Co. The advantage of this laser is that it can be supplied to military specifications so that it should be easy to certify for flight work. The dye laser that we need should be obtainable with a pump laser similiar to the one reported by Davis and co-workers. The actual design of the dye laser will have to be investigated since we want larger bandwidths and will want scan over larger wavelength ranges.

Conclusion

In the present paper we have shown that a gas release shuttle experiment can be used to determine if the C_2 and NH radicals are produced by the solar photodissociation of NH_3 and C_2H_2. The experimental detection of the

radicals can be accomplished with a Nd-Yag pumped dye laser. The Nd-Yag laser can already be supplied to military specifications and further development of dye laser appears to be technically feasible.

This work was suported under NSG 5071.

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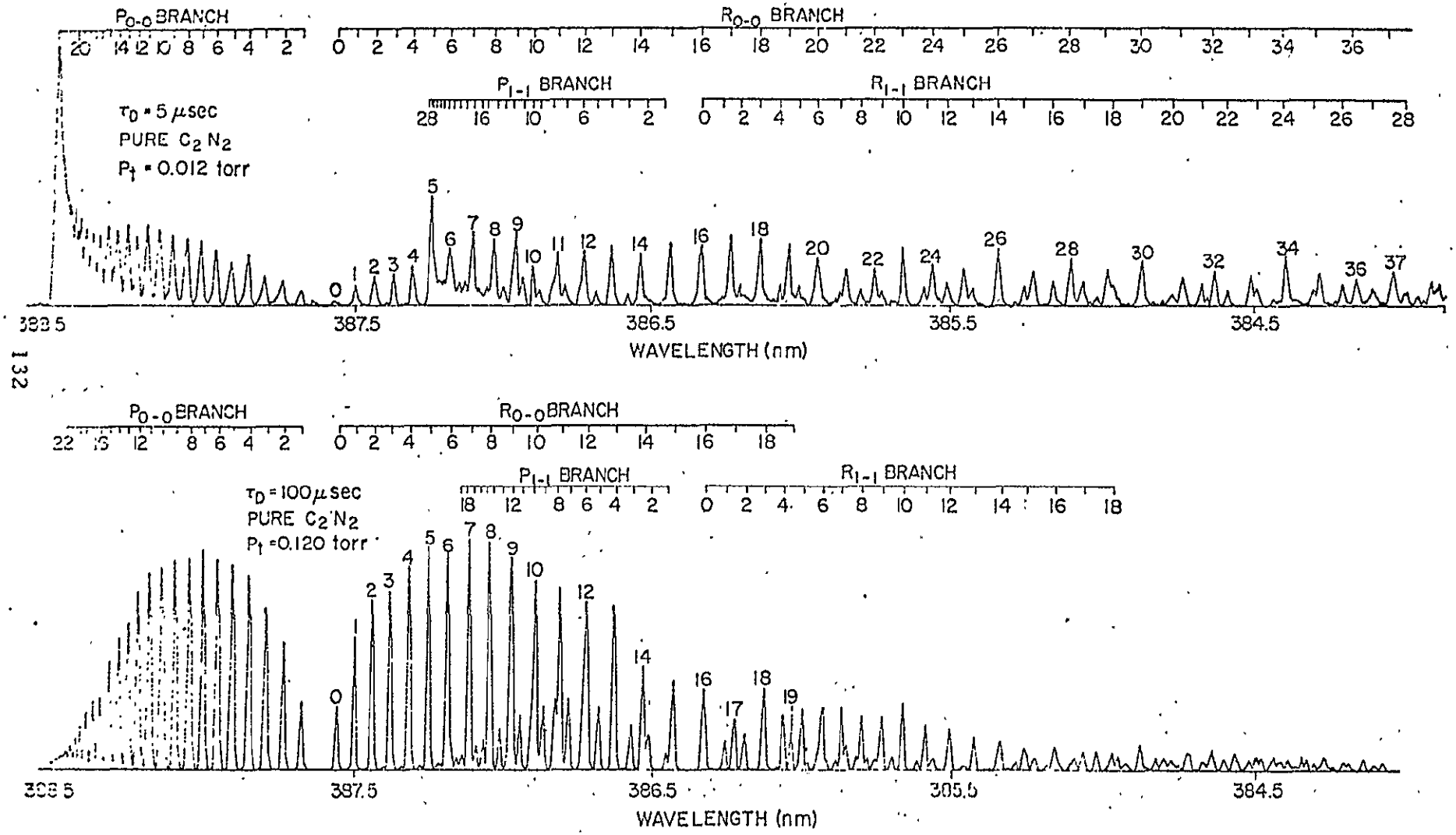

Figure 1. Laser excitation spectrum of the CN($B^2\Sigma \longleftarrow X^2\Sigma$) Violet System. The dye laser bandwidth was 0.01 nm.

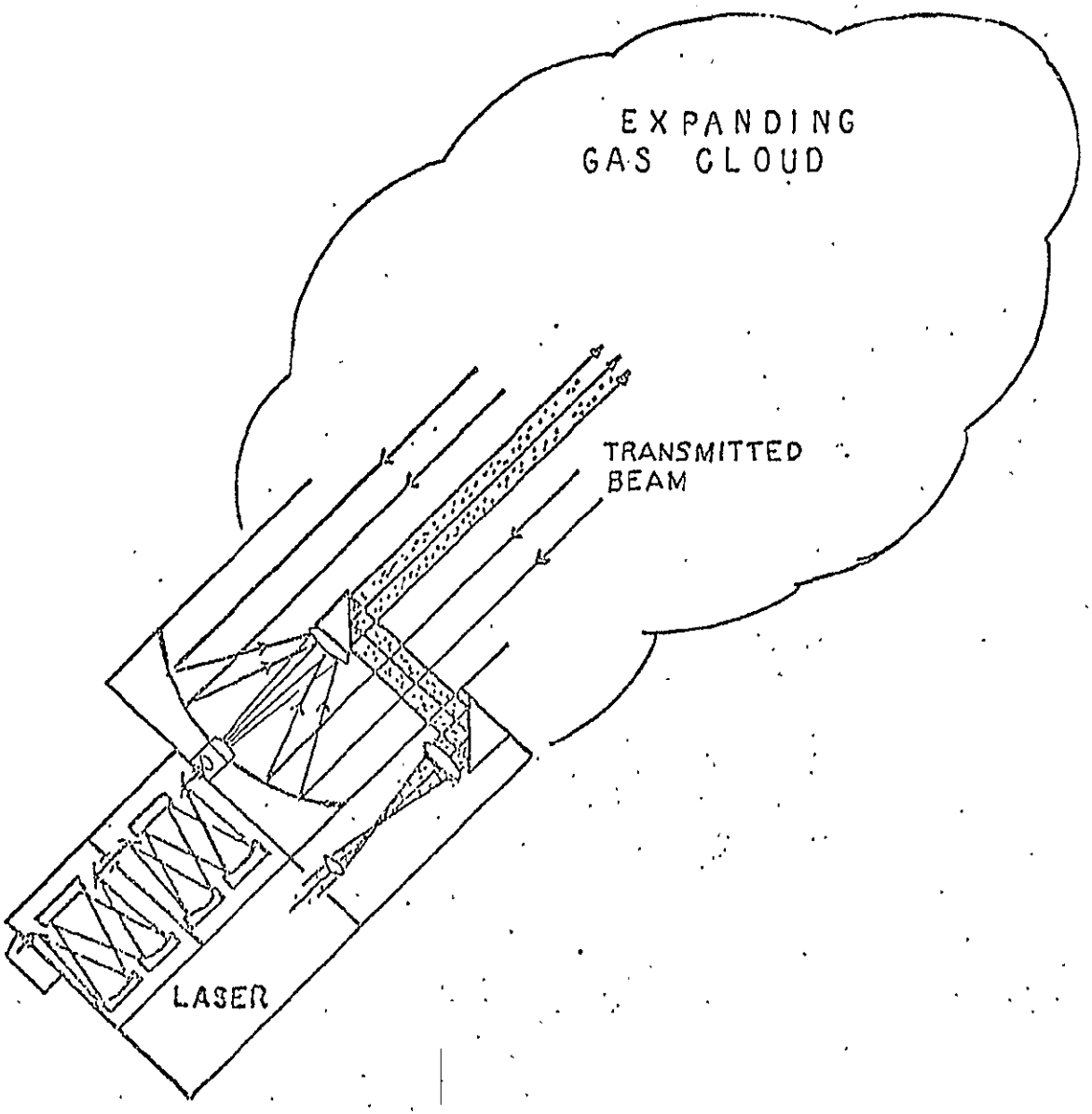

Figure 3. An example of the kind of LIDAR optical system proposed for this experiment.

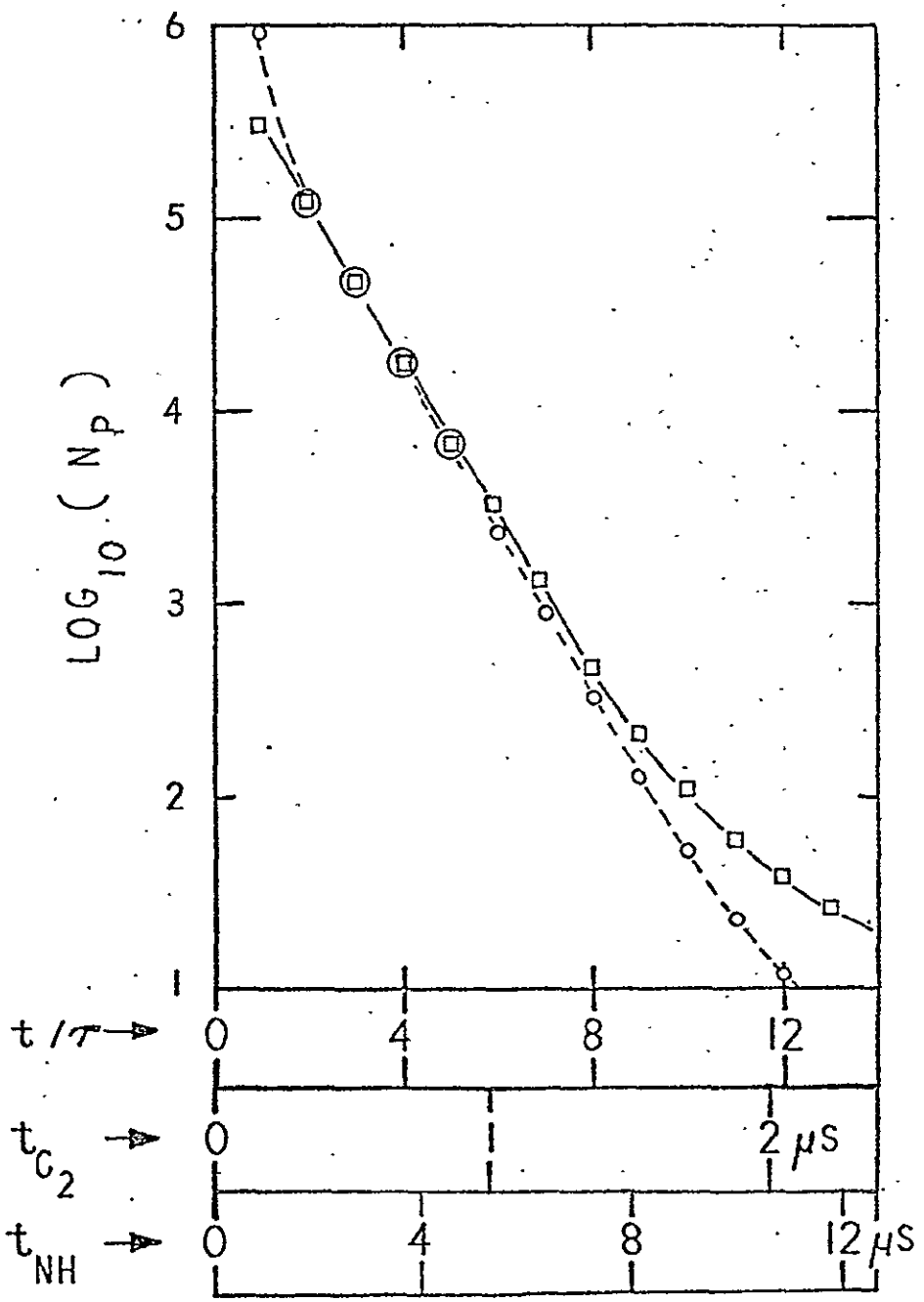

Figure 4. The calculated number of fluorescent photons striking the detector as a function of time after the laser pulse. The first time scale (t/τ) refers to the signals from both (□) C_2 and (o) NH. The two lower absolute time scales refer to the labeled radical. The signal, N_p, is per channel where the channel width equals τ.

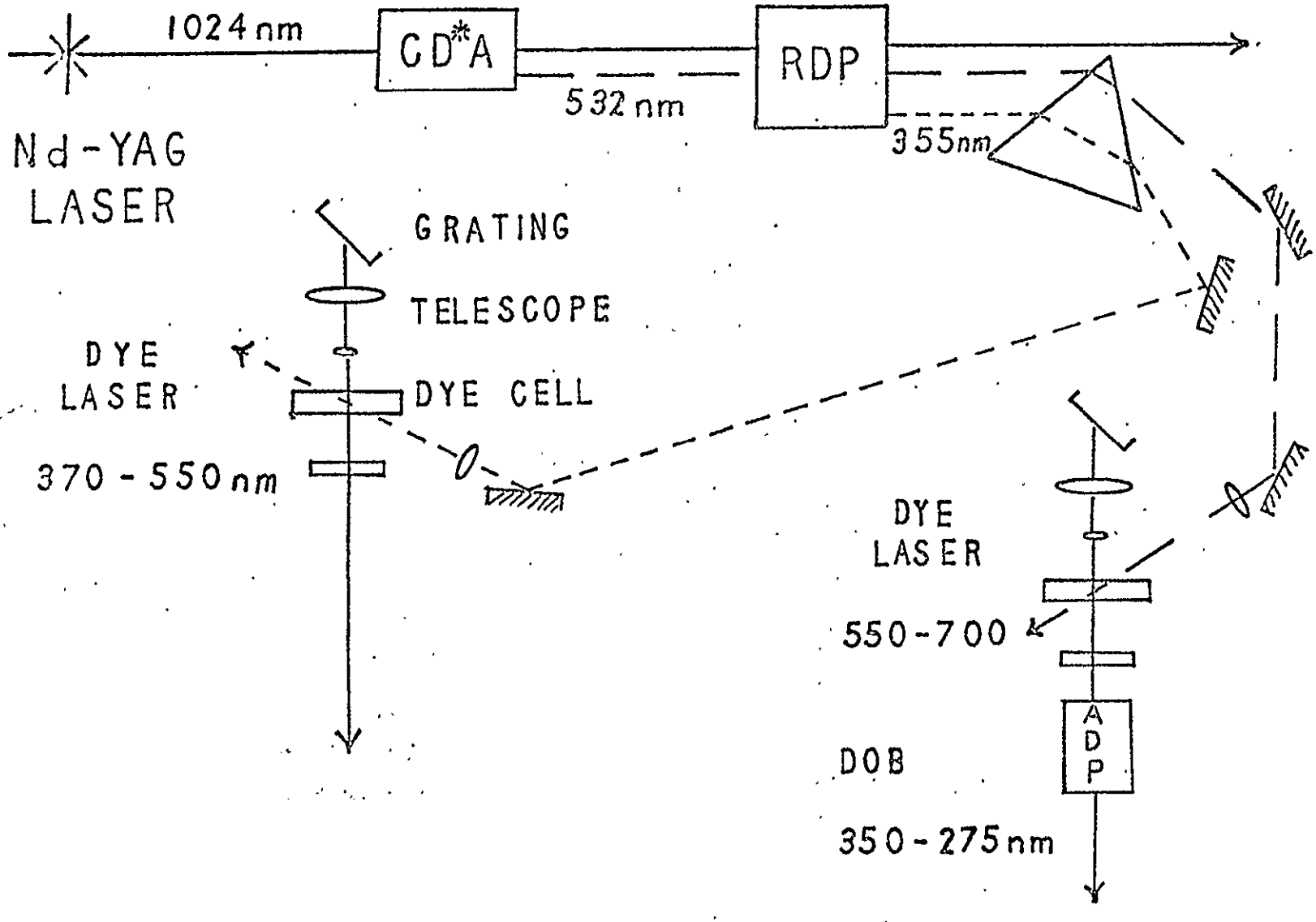

Figure 5. A possible configuration for the proposed Nd-Yad pumped doubled dye laser system.

Abstract

FLUORESCENCE SPECTROSCOPY USING THE ArF EXIMER LASER

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ArF laser illuminated NO_2 and I_2 fluoresce. The NO_2 emission is from the A state of NO fragments and requires absorption of two laser photons. I_2 Cordes band fluorescence has been resolved into two componenets in time and wavelength.

FLUORESCENT SPECTROSCOPY USING THE ArF EXIMER LASER

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The 193 nm ArF laser emission can be absorbed by many small molecules. However, because of the extremely high laser light intensity, $\sim 10^{25}$ photons/cm^2sec, the photochemical reactions observed are radically different from those seen with normal sources. We have recently presented results pointing to the dissociative simultaneous absorption of two or more laser photons by C_2N_2, C_2H_2, CH_3OH, H_2O, etc.[1] We wish to present new results confirming our interpretation.

Figure 1 shows the dispersed fluorescence from 0.4 torr of NO_2 illuminated by the ArF laser. The spectrum is dominated by a decreasing series of peaks whose wavelengths and spacings are consistant with the γ-band transitions of NO. These transitions apparently arise from vibrationally excited A state molecules of NO with $v' > 4$. A line of this series is found at 186 nm, 9 nm below the laser line. Pressure studies indicate that this line isn't the result of vibrational up-pumping. Using the thermochemical value for the dissociation energy D(NO-O) of ~25000 cm^{-1}, excitation of this line requires about 27,000 cm^{-1} more energy than a single ArF laser photon has. NO_2 provides strong evidence for multiple photon absorption through dissociative states of polyatomic molecules in the presence of a strong laser field.

We have also observed extremely intense fluorescence from the diatomic molecule I_2. The fluorescence is so intense that it can be observed in a lighted room, although only a small portion of the fluorescence

lies in the visible region. Both absorption and emission are due to the D↔X Cordes system of iodine. The fluorescence spectrum is generally the same as described by Mullikan [2] and Curtis and Evans[3], being a continuous background with a series of diffuse bands, the main set of which reach a climax at about 325 nm. Bands at higher wavelength are the result of collisional transfer to other electronic states. By using a boxcar analyzer we have been able to resolve the two components. The fluorescence is composed of a fast component concurrant with the laser pulse and a slow component, whose lifetime is about 400 ns. The fast component is responsible for a continuum emission which decreases slowly from 193 nm to beyond 400 nm. The fluorescence from the slow component gives rise to the structured diffuse fluorescence bands. Further measurements are planned on the electronic transitions induced by collision.

The ArF laser has been shown to be a ubiquitous source for dissociative excitation of polyatomic molecules by multiple photon excitation.[1] This has been reconfirmed for the case of NO_2 in this paper, and the source of radical fragment emission identified. We have also shown how the ArF laser may be used to investigate collisional electronic state transfer for the case of I_2.

This work was supported by NSG 5071 and ERDA #E-(40-1)-5056

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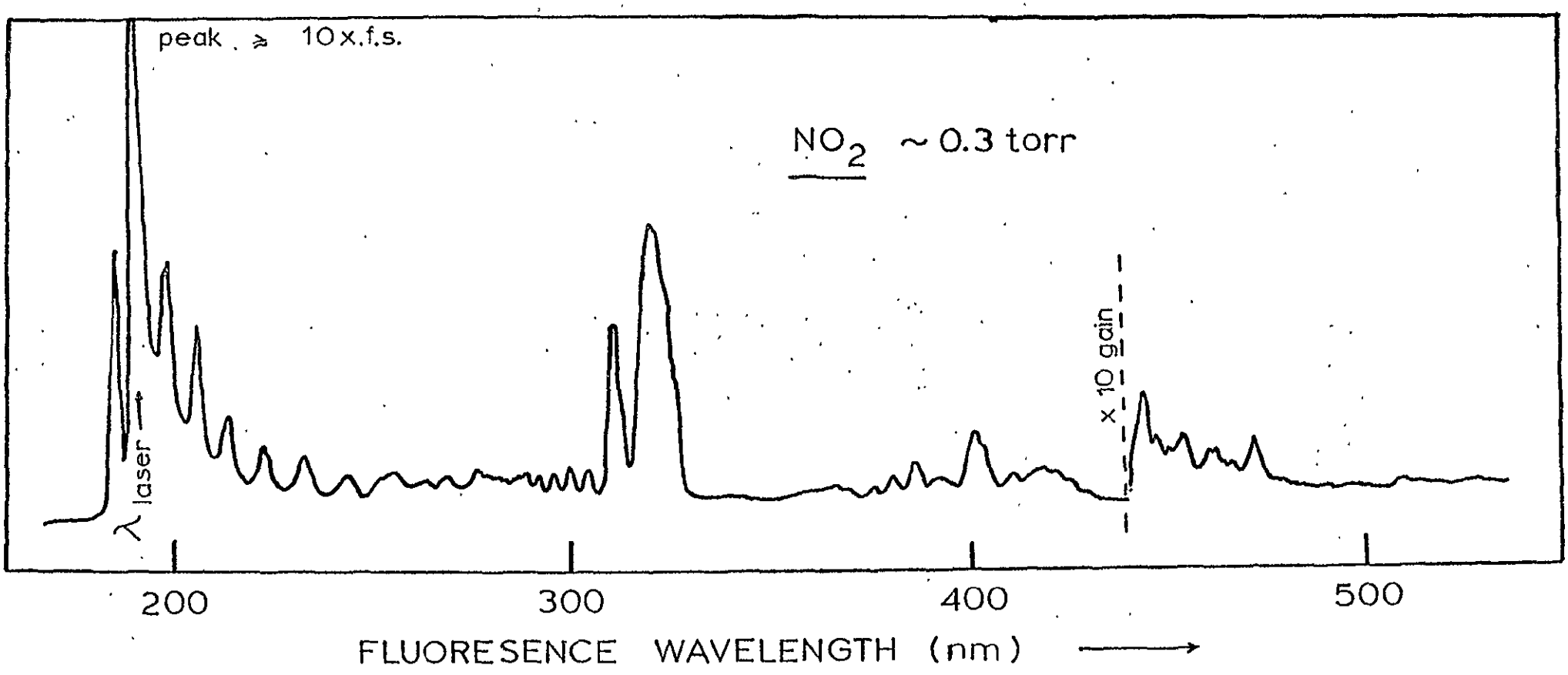
peak ≥ 10 x.f.s.
NO2 ~0.3 torr
λ laser
x 10 gain
200
300
400
500
FLUORESENCE WAVELENGTH (nm)

LASER DETECTION OF PHOTOCHEMICAL FRAGMENTS PRODUCED BY A TUNABLE VACUUM ULTRAVIOLET FLASH LAMP

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The excited electronic states of molecules are very important in determing the composition of planetary atmospheres, the behavior of optically pumped lasers, gas discharge processes, and the efficiency of laser isotope seperation schemes. In the past one of the most fruitfull techniques used in the study of the excited states of polyatomic molecules was flash photolysis combined with kinetic absorption spectroscopy[1]. This technique was used to identify any unstable molecules that result from the electronic excitation of large molecules. The limited sensitivity of absorption spectroscopy restricts the kinds of investigations that can be undertaken. Nothing could really be done in a systematic way to study the effects of variations in the energy of excitation upon the identity and quantum states of these molecules. If narrow band tunable dye lasers are used to detect these unstable molecules in fluorescence, the sensitivity of detection is greatly increased[2]. In the present work we will show how this technique may be combined with a unique tunable vacuum ultraviolet flash lamp to systematically study the effects of excitation energy upon the specific dissociation channels of the molecules.

The essential features of the apparatus have been previously described[2]. The major modification in the previous apparatus is the insertion of a specially designed holographic grating vacuum ultraviolet monochromator. The gap between the electrodes of the vacuum ultraviolet flash lamp serve as the source slit for the monochromator. The concave grating, which is corrected for astigmatism,gathers the light and refocuses onto the exit

slit of the monochromator. The light emerging from the monochromator goes directly into the fluorecence cell. One can select the wavelength of the light used to excite the molecule by tuning the monochromator. The laser induced fluorescence spectra of any fragments produced at a given wavelength is then taken. In this manner the identity and quantum state of molecular fragments can be determined as a function of the energy of excitation of the molecule under study.

An example of the type of data that can be obtained with this apparatus is given in figure 1. In this figure two laser induced spectra of the CN radical are reported. These spectra were obtained by photolyzing C_2N_2 at two different wavelengths, selected so that different vibrational bands in the excited state would be populated. These spectra clearly show the vibrational population of the CN radical increases as the excitation energy of the C_2N_2 molecule is increased. The rotational population also shows a similiar increase. This illustrates the type of fundamental information that can now be obtained. Additional examples will be presented at the conference.

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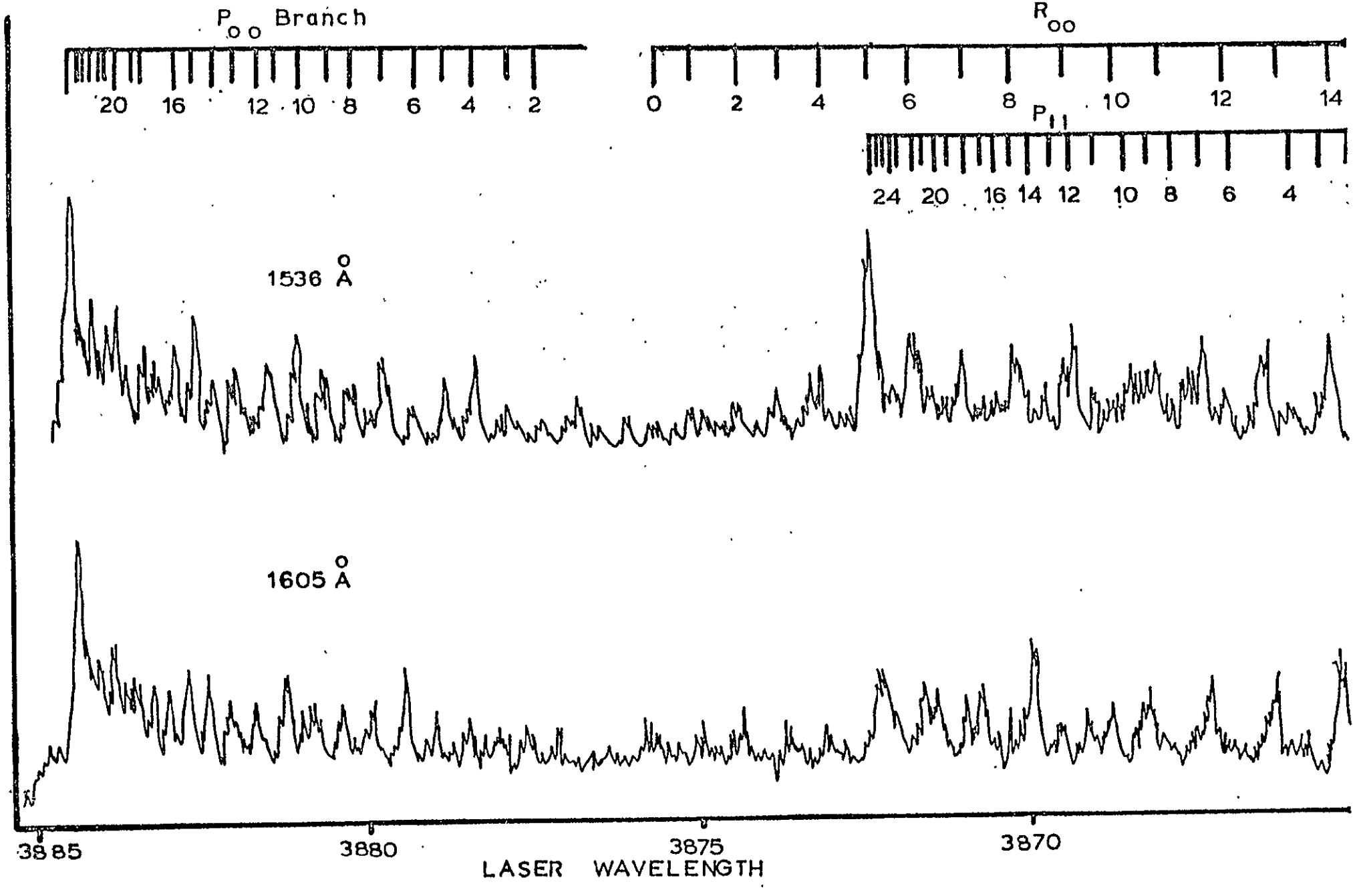
Figure Caption

Figure 1. Laser induced fluorescence spectra of the CN radical produced in the photolysis of C_2N_2 at 1536 Å and 1605 Å. The numbers refer to the rotational quantum number of the ground electronic state. The apparent noise near the band origin of the spectra obtained at 1536 Å is due to the presence of CN radicals with rotational quantum numbers of the order of 50.


P_{oo} Branch
20 16 12 10 8 6 4 2
R_{oo}
0 2 4 6 8 10 12 14
P_{11}
24 20 16 14 12 10 8 6 4
1536 Å
1605 Å
3885
3880
3875
3870
LASER WAVELENGTH

A TUNEABLE VUV PHOTOFRAGMENT MONOCHROMATOR

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Abstract

A versatile tuneable VUV photofragment monochromator, which has been constructed, is described. The instrument combines a unique flashlamp, single slit monochromator combination with laser induced fluorescent detection of the photofragments. The results of preliminary design parameter measurements are presented along with the first photofragment spectra obtained with this instrument. It is shown that the signal-to-noise ratio is adequate to assign single quantum state photofragment distributions.

INTRODUCTION

Most polyatomic molecules dissociate when they are electronically excited by VUV photons (1). The quantum state distribution of the photochemical fragments is a sensitive probe of the potential energy surface of an excited molecule. Construction of a photofragment spectrometer incorporating a tunable vacuum ultraviolet photolysis source would enable us to experimentally characterize molecular dissociation channels over an appreciable range of the potential surface. This information is necessary, as a check of existing theories of photodissociation, and as a goad to new and more detailed calculations (2). In addition, knowledge of the photofrgment energy distributions are important to our understanding and modeling of such diverse problems as the composition and kinetics of planetary atmospheres, the behavior of optically pumped lasers and laser chemistry schemes.

In the past, flash photolysis was combined with kinetic absorption spectroscopy to allow investigators to detect unstable photodissociation fragments from polyatomic molecules (1). Unfortunately, the detection method is extremely insensitive and because of the associated loss of intensity, one cannot study the effect of varying the photolysis wavelength by passing the broad band exciting light through a VUV monochromator.

Kent Wilson and colleagues combined a powerful laser, used as the photolysis light source, with mass spectrometric detection of the fragments (3). They used this photofragment spectrometer to measure the recoil energy of the radicals, and by varying the laser polarization they were able to determine the excited state's symmetry. This method requires an intense laser source to obtain reasonable signal-to-noise ratios. Since there are currently no intense tunable dye laser sources in the VUV the requirement implies that little systematic information can be acquired with Wilson's method.

The intense laser source can further complicate the results by causing some multiphoton processes (4). Moreover, as only translational energy distribution are measured, quantum state distributions must be inferred.

Jackson and Cody have reported the use of a broad band VUV flash lamp as a photolysis source together with laser induced fluorescence detection of ground state radicals, to measure the energy distribution of photochemical fragments (5). In this case the broad band excitation makes it difficult to unamiguously assign the photon energy that excites the molecules. McDonald and co-workers solved this problem by combining the laser detection with laser a photolysis source (6). Their results and those of Cody and Sabety-Dzvonik (7), and Ling and Wilson (8) on the photodissociation of ICN stimulated some recent theoretical work by Freed, et al (2), but again the possibilities are limited by fixed frequency photolysis sources.

In the present paper we will describe how a flashlamp with a single slit astigmatic high throughput VUV monochromater can be combined with laser induced fluorescence detection, to construct a tunable vacuum ultraviolet photofragment spectrometer. This instrument has been used to selectively dissociate cyanogen and measure the fragment quantum state distribution as a function of incident photon energy.

While the detection method has become standard in recent years, the photolysis source incorporates several unique features. These distinguishing characteristics include a thyratron triggered resonant charging circuit to achieve high average power from the flashlamp and match its operating rate to the most efficient repetition rate of the dye laser system. The flashlamp electrodes are used as the entrance slit for the monochromator. This eliminates intensity losses associated with imaging and/or aperturing of the light source on the monochromator entrance slits. The monochromator uses a simple symmetric mount with only one reflecting surface. Normally this

type of mount is corrected for abberations at one wavelength, resulting in a considerable loss of light at other wavelengths. This difficulty can be overcome by using a holographic grating.

EXPERIMENTAL APPARATUS

The experimental apparatus is shown in Fig. 1. It consists of three main assemblies: the photolysis light source, the experimental cell with its vacuum system and the dye laser detection system. The light source is a flashlamp, pressurized to ~2 atm with slowly flowing argon. The flashlamp electrodes, which confine the discharge, act as the entrance slits for a VUV monochromator (9). They are carefully gapped and sit at the focal point of the 2" by 2" holographic grating. The effective focal length of this arrangement is 200 mm and the aperture ratio is f/4.5 The entrance and exit arms of the monochromator are sealed by 2 inch diameter, 2 mm thick MgF_2 windows and a high vacuum is maintained by a Varian 8 l/sec ion pump.

This simple mounting collects 0.4 per cent of the flashlamp light while the holographic grating practically eliminates astigmatism. For comparison, because of astigmatism, the use of a ruled grating with the same size slits would result in a six-fold reduction in transmitted light.

To obtain high average power and match the most efficient operating condition of the dye laser, a voltage doubling resonant charging circuit for the flash lamp was built. This circuit is shown in Fig. 1. The thyratron trigger is used as a reliable switch for firing of the flashlamp. By using resonant charging, at rates up to 16 Hz, 10 joules of energy per pulse can be stored in the 0.05 μf capacitor with the 10 k.v., 100 ma power supply. The flashlamp, flashlamp power supply, and triggering circuit assembly are all housed in a Faraday cage so as to minimize RF interference. The only break in the cage is a filtered 110 v line to provide power. The lamp is triggered by a free running oscillator and the light flash passes through a piece of fine copper screening, thus there are no output or input lines

: holes in the cage.

The fluorescence cell and dye laser detection system are similar to ıose described in Ref. 5. The gas handling system allows for freeze-thaw ırification of gases and gas mixing. With a standard pumping stack, final ressures of $1x10^{-6}$ torr are achieved and the pressure in the sealed fluo- escence cell rose less than $1x10^{-4}$ torr in a half hour period.

The detection system is based upon a Molectron N_2 pumped tunable dye aser. The laser light enters the cell through long baffle arms, inter- ecting the photolysis light 6 cm from the exit slit. The radicals hat have been formed by photodissociation are excited by this laser beam. hen these radicals radiate, the fluorescent light is spatially and chroma- :ically filtered by using a Jobin-Yvon H-20 V monochromator as a broadband :ilter. A 9813 QB EMI photomultiplier is mounted behind the H-20 monochro- ıator. The electrical signal from this tube is measured with a PAR 160 ›oxcar analyzer and recorded on a strip-chart recorder that moves synchro- ıously with the dye laser scanning mechanism.

The lamp is triggered by a free running EGG TM-27 thyratron trigger generator. A 1P28 photomultiplier views scattered visible light from the flashlamp and fires a discriminator. This discriminator pulse, which is synchronous with the lamp pulse, drives a variable delay generator whose outputs trigger both the boxcar analyzer and the nitrogen laser.

A pyroelectric joulemeter, is used to monitor the intensity of the laser beam after it passes through the fluorescence cell. This is connected to a second boxcar analyzer. The relative dye laser intensity is also re- corded on a strip-chart recorder.

SYSTEM DIAGNOSTICS

The time and wavelength characteristics of the flashlamp-monochromator combination were measured by letting the light from the exit slit strike a

sodium salicylate window. The fluorescent light is detected by a R818 Hammatsu photomultiplier. The response of this detector is independent of the wavelength of the VUV radiation. Time dependences of the light coming from the flashlamp were observed on a fast oscilliscope. The FWHM of the light pulse is ~100 ns. The relative intensity of the light as a function of wavelength is shown in Fig. 2. This was obtained by scanning the monochromator and measuring the R818 signal with a picoammeter.

The output of the photolysis source is uniform from 220 nm to 160 nm. Below this the output drops steeply until it reaches the MgF_2 cutoff at about 120 nm. Earlier work by Tanaka et. al. using a high pressure continum rare gas lamp suggests that our argon lamp should be relatively flat from 150 nm down to about 110 nm. (10). This seeming contradiction may be resolved by considering the transmission losses of a 4 mm piece of MgF_2. The dashed line in Fig. 2 is the absorbance of the window material which closely follows the observed falloff. (11) This suggest that the use of thinner windows or a different window material could result in higher outputs at the short wavelengths.

The wavelengths of the monochromator flashlamp source was calibrated by measuring the absorption of Xe in the fluorescence cell. The signal on the photomultiplier was maximized by adjusting the flashlamp relative to the grating in both the vertical and the horizontal directions. After this adjustment was made the absorption of Xenon at 147.0 and 129.6 nm were found to occur at 146.7 and 129.9 nm respectively.

The approximate intensity of the light being emitted by the monochromator-flashlamp combination was estimated in two ways. First an attempt to measure the amount of H_2 formed as a result of the vacuum ultraviolet photolysis of the ethylene proved negative. This places an upper limit on the intensity of the light source of about 5×10^{11} photons/pulse. Another estimate

of the intensity of the light source may be made from the average photo current measured with the sodium salicylate window. This calculation also yields a light intensity of 5×10^{11} photons/pulse, in reasonable agreement with the previous estimate. Since the exit slit is .02 cm wide and the image is about 1.0 cm high, the calculated intensity of the light at the slit is 1×10^{20} photons/cm^2 sec for a 8.0 nm bandwidth

In order to test the photofragment spectrometer C_2N_2 was used. The gas is purified and introduced into the fluorescence cell at pressures from 15 to 150 mtorr. Under these conditions the C_2N_2 is always optically thin. The laser was delayed from 2 to 100 μ sec with respect to the flashlamp. At both low pressures and short delays the unrelaxed rotational and vibrational states are observable. The results obtained using a 2μsec delay and 50 mtorr of C_2N_2 are shown in Fig. 3. These results show that under these conditions the ground state radicals have not had time to relax before they are detected. They also show that monochromator-flashlamp combination can produce radicals with a different ro-vibronic distribution when different vibrational levels of the excited of C_2N_2 are populated. A detailed analysis of this data will be deferred to a later paper.

The overall efficiency of the new system may be measured by comparing the photofragment signal obtained with the unfiltered flashlamp to the signal obtained using the monochromator in the zeroth order. These results are reported in Fig. 4. They show that the flashlamp monochromator combination results in a ten fold reduction of the signal. The manufactures specification of the reflectivity of the grating is 20% which accounts for most of the reduction. Some additional losses may be attributed to the transmission losses in the MgF_2 window.

CONCLUSION

It has been demonstrated that a specially designed tunable VUV light source can be used as a photodissociation source for studying the effects of excitation energy upon energy partitioning among photochemical fragments. Although the source does not produce copious amounts of radicals we are able to detect them with a reasonable signal to noise ratio because of the sensitivity of the laser fluorescence detection method.

This work was supported by a NASA grant, number NSG 5071.

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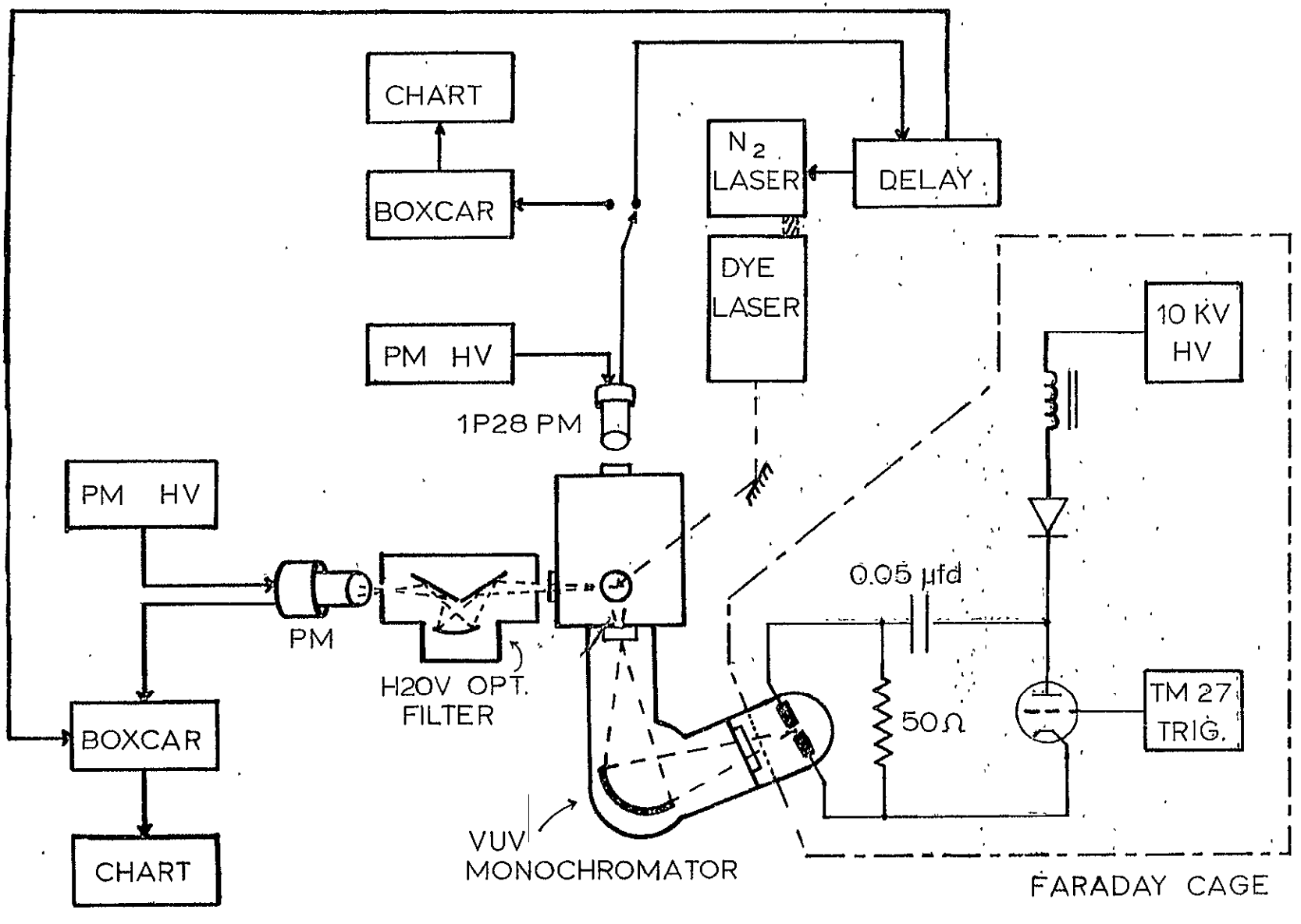
FIGURES

Figure 1. : The experimental apparatus. The flashlamp and flashlamp power supply are shown on the right, enclosed in a Faraday cage. The signal detection electronics are on the left side of the diagram. The photomultiplier that faces into the output of the VUV monochromator may be used either to measure the wavelength characteristic of the photolysis source (switch to the left), or to synchronize the dye laser and the boxcar analyzer to the flashlamp light pulse.

Figure 2. : The solid line shows the relative intensity light coming from the flashlamp - VUV monochromator combination as a function of wavelength. The dashed line shows the transmission of 4 mm of MgF_2 as a function of wavelength (11).

Figure 3. : Photofragment spectra obtained with irradiation of 154 and 160 nm in cyanogen. The pressure of cyanogen was 50 mtorr and the delay between flashlamp and laser was 2 μs. Both spectra are vibrationally and rotationally unrelaxed.

Figure 4. : Photofragment spectra of 100 mtorr of cyanogen at 100 μs delay between flashlamp and laser firings. Diagram 4a shows spectra taken with the flashlamp attached directly to the reaction cell. Diagram 4b shows spectra taken with the VUV monochromator in position between the flashlamp and the cell and tuned to zeroth order. Note the scale change of a factor of 10 between the two figures.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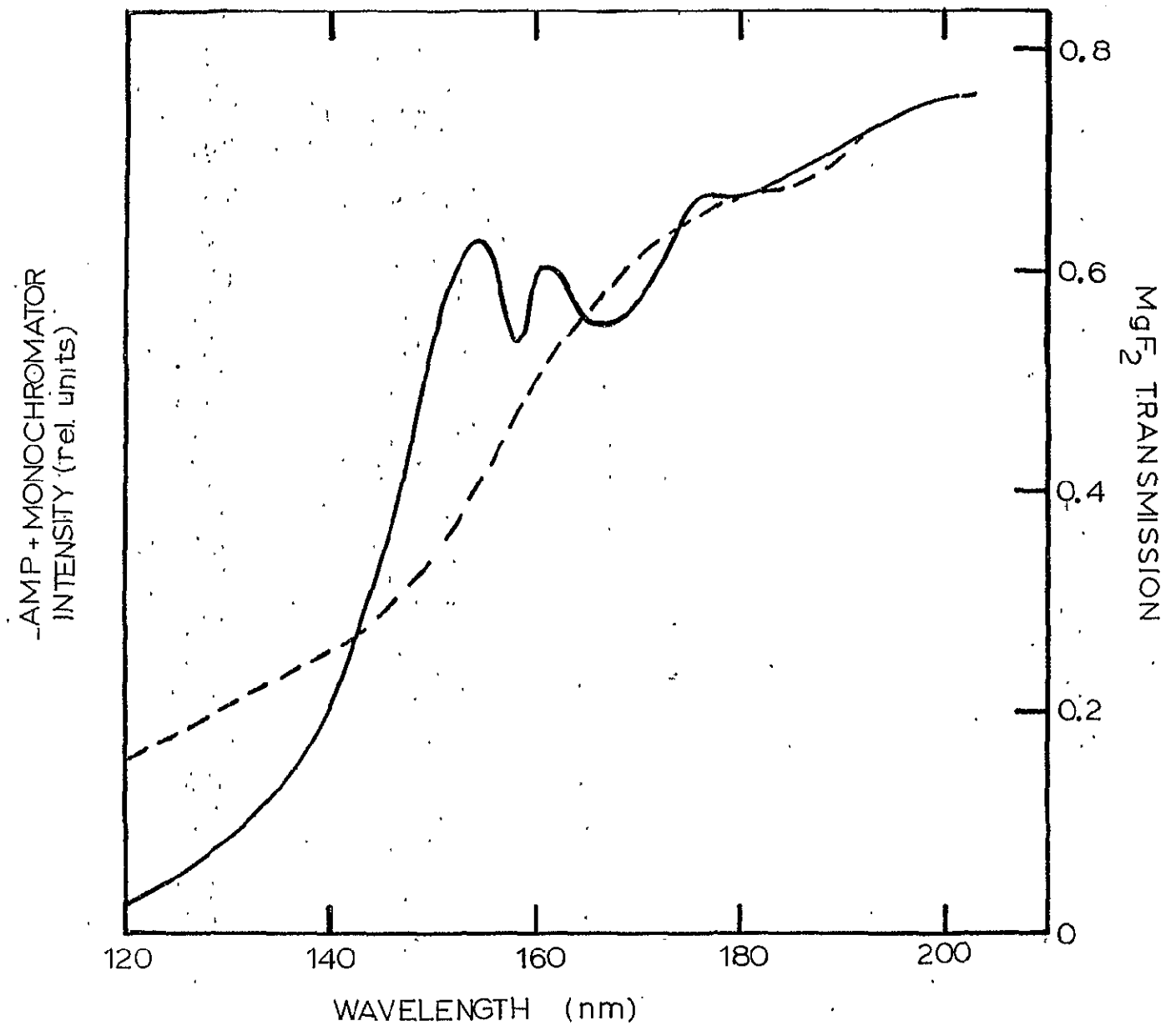
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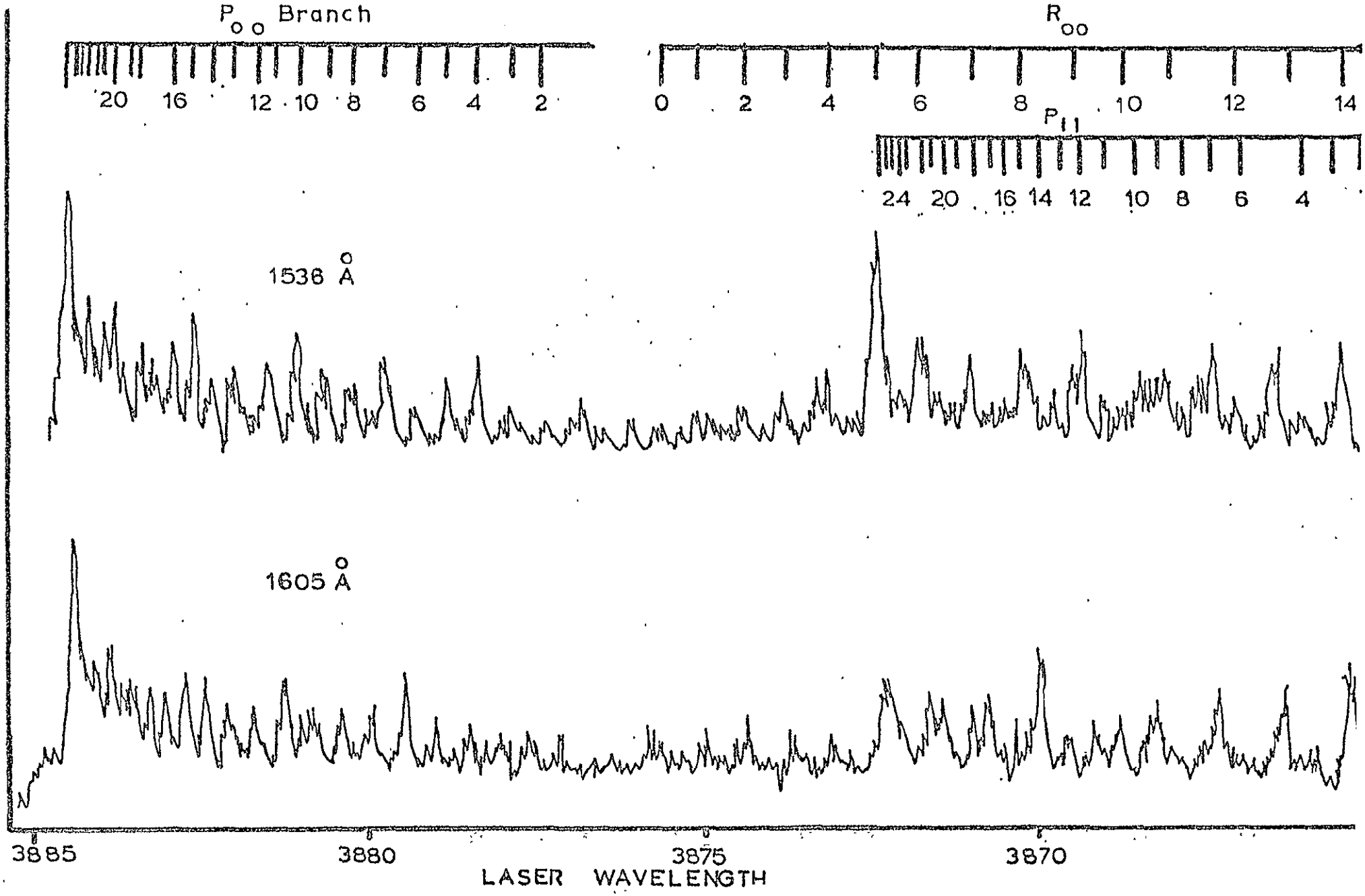
AMP + MONOCHROMATOR
INTENSITY (rel. units)
MgF2 TRANSMISSION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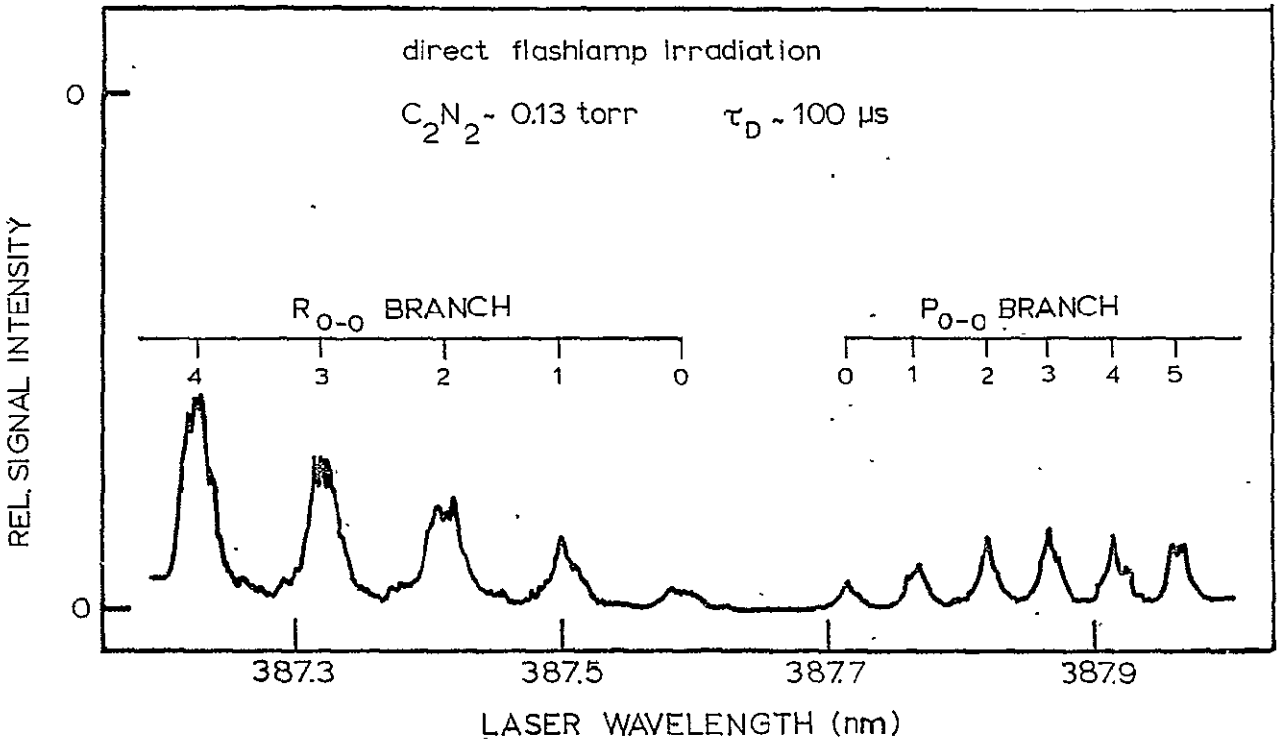
LASER WAVELENGTH


direct flashlamp irradiation
C_2N_2 ~ 0.13 torr
τ_D ~ 100 μs
R_{0-0} BRANCH
P_{0-0} BRANCH
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0
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REL. SIGNAL INTENSITY
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387.5
387.7
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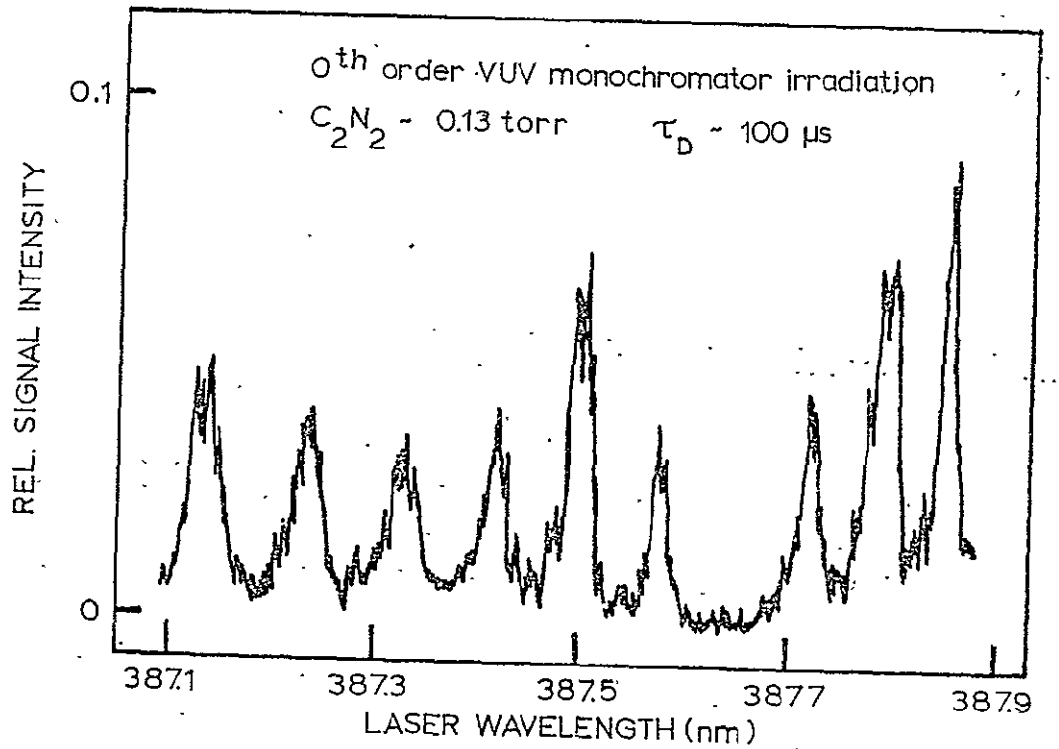
LASER WAVELENGTH (nm)


0th order VUV monochromator irradiation
C_2N_2 ~ 0.13 torr
τ_D ~ 100 μs
0.1
0
REL. SIGNAL INTENSITY
387.1
387.3
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387.7
387.9
LASER WAVELENGTH (nm)